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SOME DOUBLE HALIDES OF CADMIUM WITH THE METHYLAMINES AND TETRAMETHYLAMMONIUM.[1]

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The results obtained in investigations of the double halides formed by halides of the heavy metals and those of ammonium led to experiments with substituted ammonias, and the work of Slagle[2] and Base,[3] with aniline and the toluidines, has been extended in this investigation to a study of the compounds formed by the methylamines and tetramethylammonium. The following double halides of cadmium with the halides of the alkali metals and ammonium are recorded in the literature.

1 : 1	2 : 1
$(NH_4)CdBr_3, \frac{1}{2}H_2O$	$(NH_4)_2CdCl_4, H_2O$
NH_4CdF_3	$(NH_4)_2CdI_4, 2H_2O$
$NaCdBr_3, 2\frac{1}{2}H_2O$	$Na_2CdCl_4, 3H_2O$
$KCdCl_3, \frac{1}{2}H_2O$	K_2CdCl_4
$KCdBr_3, \frac{1}{2}H_2O$	K_2CdCl_4, H_2O
$CsCdCl_3$	$Na_2CdI_4, 6H_2O$
$CsCdBr_3$	$K_2CdI_4, 2H_2O$
$CsCdI_3, H_2O$	Cs_2CdCl_4
	Cs_2CdBr_4
	Cs_2CdI_4
	Rb_2CdCl_4

[1] From the author's dissertation submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1897. The work was undertaken at the suggestion of Professor Remsen, and was carried on under his guidance.

[2] This JOURNAL, **20**, 633.

[3] *Ibid.*, **20**, 646.

3 : 1	4 : 1
Cs_3CdBr_5	$(NH_4)_4CdCl_6$
Cs_3CdI_5	$(NH_4)_4CdBr_6$
	K_4CdCl_6
	K_4CdBr_6

Preparation of Material.

Cadmium chloride and cadmium iodide were prepared by dissolving the metal, previously tested for purity, in the respective acids and evaporating the solutions to dryness.

Inasmuch as cadmium dissolves quite slowly in hydriodic acid, in a subsequent preparation of the iodide, cadmium oxide was used. This was prepared by igniting the oxalate, which was precipitated from a solution of cadmium nitrate by oxalic acid. Cadmium bromide was prepared first by heating the metal in a combustion tube and passing bromine vapor over it, the bromide subliming to the cooler part of the tube. However, it was found later to be more convenient to dissolve the metal in bromine water. The bromine in both cases was purified by distillation from potassium bromide.

The hydrochlorides of the methylamines (Bender and Hobein's preparations) were used as the sources of the bases.

Tetramethylammonium hydroxide was prepared from the iodide by Hofmann's original method.[1] A moderately dilute solution of the iodide was gently warmed, and shaken up with moist silver oxide until further additions of the dark-brown oxide were no longer changed to the yellow silver iodide. The solution was then filtered and afterwards found to be free from iodine.

The bases were neutralized with the required acids, and the solutions were then concentrated to a convenient bulk.

Methods of Analysis.

The objections which Muspratt[2] raises to the established method of determining cadmium were not confirmed by my experience.

Preliminary experiments were made in which cadmium, known to be very pure, was used. A weighed quantity was

[1] Ann. Chem. (Liebig), **78**, 263.
[2] J. Soc. Chem. Ind., **13**, 211.

dissolved in hydrochloric acid and the solution was diluted to a known volume. Portions were drawn off and analyzed. In every case the analyses were perfectly satisfactory.

The method used in determining cadmium was as follows: Dilute solutions were heated to a temperature near boiling, and a strong solution of potassium carbonate was added, drop by drop, with constant stirring. After boiling a few minutes and allowing the beaker to stand, the whitish translucent precipitate of basic cadmium carbonate settled to the bottom, leaving the supernatant liquid perfectly clear.

A Gooch crucible was used in all cases for filtration. After washing several times by decantation, the precipitate was thrown on the filter and washed with several hundred cc. of boiling water. The Gooch crucible, without a cap, was then placed on a platinum plate in an iron crucible, dried at a moderate heat, and heated to dull redness for ten or fifteen minutes.

The halogens were determined by the volumetric methods of Mohr and Volhardt, and gravimetrically. When the silver halides were weighed, a Gooch crucible was used, and the precipitate was dried in an air-bath at 140°.

Preparation of the Double Salts.

Concentrated solutions of the two salts were made, and from the calculated amounts present in each, such volumes of the two solutions were taken as to vary the molecular proportions in the different beakers, thus:

1 : 1; 1 : 2; 1 : 3; 1 : 4; 2 : 1; 3 : 1; 4 : 1.

Other proportions were used in cases which seemed to justify the use of solutions of greater proportional difference. The mixtures were acidulated with the corresponding acid, and put in vacuum desiccators over sulphuric acid and caustic soda. The successive crops of crystals were analyzed as long as they appeared homogeneous. The microscope was constantly used to ascertain this.

Further particulars will be noted in the descriptions of the individual double salts.

Compounds Described.

2 : 1 Methylamine chlorcadmiate.
1 : 1 Methylamine bromcadmiate.
2 : 1 Methylamine bromcadmiate.
1 : 1 Dimethylamine chlorcadmiate.
1 : 2 Dimethylamine chlorcadmiate.
3 : 2 Dimethylamine chlorcadmiate.
1 : 1 Dimethylamine bromcadmiate.
2 : 1 Dimethylamine bromcadmiate.
1 : 4 Dimethylamine bromcadmiate.
1 : 1 Dimethylamine iodocadmiate.
1 : 1 Trimethylamine chlorcadmiate.
3 : 2 Trimethylamine chlorcadmiate.
1 : 1 Trimethylamine bromcadmiate.
3 : 2 Trimethylamine bromcadmiate.
1 : 1 Trimethylamine iodocadmiate.
2 : 1 Trimethylamine iodocadmiate.
1 : 1 Tetramethylammonium chlorcadmiate.
1 : 1 Tetramethylammonium bromcadmiate.
2 : 1 Tetramethylammonium bromcadmiate.
1 : 1 Tetramethylammonium iodocadmiate.
2 : 1 Tetramethylammonium iodocadmiate.

METHYLAMINE SALTS.

Double Chlorides.

2 : 1 Methylamine Chlorcadmiate.—When solutions of cadmium chloride and methylamine hydrochloride are mixed so that the number of molecules of the former to that of the latter bear these ratios: 2 : 1; 1 : 1; 1 : 2; 1 : 3; 1 : 4; the same double salt crystallizes out in every case.

Usually three or four successive crops of crystals from each beaker were obtained. The crystals are tabular, transparent, with a fibrous fracture, resembling selenite in general appearance. The cleavage is perfect, parallel to the broad faces, giving thin, pearly, flexible laminae.

Unsuccessful efforts were made to get specimens for crystallographic work. The general appearance of the crystals would indicate that they are isometric in form.

The solutions from which these crystals were obtained were very concentrated. The mother-liquor was drained off as thoroughly as possible, and the crystals quickly washed with water, pressed between layers of smooth drying-paper, and dried in the air.

The analyses were quite concordant.

From beakers in which cadmium chloride was in a large excess, there were some indications of another double salt, when the solution was evaporated nearly to dryness. Under the microscope were noticed very small rod-shaped crystals in company with the silky needles of cadmium chloride. It was found impossible to get this salt in a pure form for analysis. When water was added to the syrupy mass of mixed crystals and concentrated mother-liquors, the crystals were at once dissolved.

I. 0.1518 gram salt gave 0.2730 gram AgCl.
0.3151 gram salt gave 0.1262 gram CdO.

II. 0.0811 gram salt gave 0.1463 gram AgCl.
0.1498 gram salt gave 0.0601 gram CdO.

	Calculated for $[NH_3(CH_3)]_2CdCl_4$.	Found. I.	II.
Cl	44.55	44.42	44.55
Cd	35.24	35.04	35.10

Double Bromides.

1 : 1 Methylamine Bromcadmiate.—This salt is so easily soluble that it was difficult to get it sufficiently pure for analysis. From solutions in which cadmium bromide was in the ratios 1 : 1, 2 : 1, 3 : 1, etc., to the hydrobromide of the amine, long flattened prisms with rectangular terminations were obtained. The crystals were transparent, generally very much striated, and little could be determined as to their crystal form. The very concentrated mother-liquors from which they crystallized were always colored more or less with free bromine. In order to get the salt in a pure condition, it was found necessary to get it in sufficient quantities to permit of a hasty washing. By this very wasteful process enough was obtained for analysis in two instances. Other estimations of cadmium were sufficiently close to show what the salt was.

I. 0.3040 gram salt gave 23.65 × 0.00801 Br.
0.3040 gram salt gave 0.1038 gram CdO.
II. 0.2240 gram salt gave 0.3319 gram AgBr.
0.2766 gram salt gave 0.0957 gram CdO.

	Calculated for $[NH_3(CH_3)]CdBr_3$.	Found. I.	II.
Br	62.41	62.30	62.97
Cd	29.23	29.95	29.87

2 : 1 Methylamine Bromcadmiate.—From solutions of methylamine hydrobromide and the metallic bromide mixed in the proportions 2 : 1, 3 : 1, 4 : 1, respectively, there separated from the syrupy liquid, on concentration, large tabular crystalline masses, the edges of which were fringed with dendritic forms. No well-defined individual crystals were obtained. Little trouble was experienced in getting this salt in a pure condition for analysis, and a number of concordant results were obtained.

I. 0.3593 gram salt gave 0.0932 gram CdO.
0.3552 gram salt gave 0.5394 gram AgBr.
II. 0.2860 gram salt gave 0.0746 gram CdO.
0.2249 gram salt gave 18.09 × 0.00801 Br.

	Calculated for $[NH_3(CH_3)]_3CdBr_4$.	Found. I.	II.
Cd	22.58	22.69	22.79
Br	64.51	64.54	64.42

Double Iodides.

Solutions of methylamine hydroiodide and cadmium iodide were mixed in the usual proportions and allowed to evaporate slowly.

In the beakers containing cadmium iodide in large excess, this salt crystallized out unchanged. In the other beakers, after the solutions had nearly reached dryness, a mixture of exceedingly soluble crystals was obtained. It was found impossible to effect a separation by mechanical means. The shiny hexagonal plates of cadmium iodide were easily recognized. Among these were some transparent crystalline aggregates of a different order of crystallization from the latter. Some of these were separated and dried as well as possible on filter-paper. Qualitative experiments showed the presence of considerable quantities of cadmium.

DIMETHYLAMINE SALTS.

Double Chlorides.

1 : 1 Dimethylamine Chlorcadmiate.—This salt is readily obtained from very concentrated solutions of dimethylamine hydrochloride and cadmium chloride mixed in the molecular proportions 1 : 1, 2 : 1, and 1 : 2, respectively.

The crystals obtained under different conditions differ markedly in appearance. The forms most frequently met with were long, striated, flattened prisms, obliquely terminated. Some large flattened rhombohedral prisms crystallized from a solution which was slowly evaporated for several months. Some of these were over two inches long.

Owing to the extremely concentrated solutions from which this salt comes down, the analyses in many instances were not very sharp.

However, recrystallized specimens gave results quite close to the theoretical. When heated to about 180° this salt sublimes slightly, at 240° it begins to darken, and at 261°–262° it melts quite sharply with signs of decomposition.

I. 0.5064 gram salt gave 0.2461 gram CdO.
0.2780 gram salt gave 0.4516 gram AgCl.

II. 0.1521 gram salt gave 0.0733 gram CdO.
0.2075 gram salt gave 0.3368 gram AgCl.

	Calculated for $[NH_3(CH_3)_2]CdCl_3$.	Found. I.	II.
Cd	42.36	42.52	42.16
Cl	40.17	40.12	40.09

1 : 2 Dimethylamine Chlorcadmiate.—This salt in general appearance is somewhat similar to the last-described double halide; however, its flattened, lath-shaped, transparent crystals are not so obliquely terminated. It comes down from concentrated mixtures of solutions of the two constituents in which cadmium chloride is in excess. From a mixture in the ratio 1 : 2, one crop of crystals of the 1 : 1 salt was obtained. The successive crops were the 1 : 2 salt.

The salt was drained as thoroughly as possible from mother-liquors, quickly washed with water, and pressed between folds of smooth drying-paper. As it was found to be slightly efflorescent, it was not air-dried, but weighed immediately.

The apparatus used for determining water of crystallization consisted of an air-bath through which was extended a piece of combustion tube. At either end were U-tubes containing glass beads moistened with sulphuric acid. Dried air was drawn over the salt which was placed in a porcelain boat in the tube.

A constant weight was obtained with the salt in question after heating for one hour at 110°. No further loss was noted on raising the temperature to 125°. At 170° there were signs of sublimation in the cold parts of the tube, but the loss in weight of the salt was very small. No signs of decomposition were apparent at 270°, when it was heated in a melting-point capillary tube.

I. 0.2466 gram salt gave 0.1412 gram CdO.
0.1092 gram salt gave 0.1739 gram AgCl.
0.6818 gram salt lost 0.0512 gram H_2O at 110°.

II. 0.1291 gram salt gave 0.0738 gram CdO.
0.2093 gram salt gave 0.3341 gram AgCl.
1.3653 grams salt lost 0.1026 gram H_2O at 110°.

	Calculated for		Found.	
	$[NH_3(CH_3)_2]Cd_2Cl_4.2H_2O$.	$[NH_3(CH_3)_2]Cd_2Cl_4$.	I.	II.
Cd	....	50.06	50.10	50.01
Cl	....	39.56	39.33	39.42
H_2O	7.44	....	7.50	7.52

3 : 2 Dimethylamine Chlorcadmiate.—From mixed solutions of the constituent halides made up in the proportions 2 : 1, 3 : 1, and 4 : 1, dimethylamine hydrochloride being in excess, no crystals appeared until evaporation had proceeded nearly to dryness.

The crystal forms usually met with under these circumstances were flat, transparent prisms having a rectangular cross-section, the corners of which were symmetrically truncated. The solution at this stage of concentration was syrupy in its consistency. After draining off the mother-liquors as thoroughly as possible, the crystals were washed with water. This seemed to cause a slight superficial decomposition, the transparent crystals being rendered somewhat translucent.

Inasmuch as salts of analogous composition have not been met with hitherto, it was thought at first that the presence of

impurities had affected the analyses. Comparing the results obtained with the formula given below, it was found that the figures for chlorine were always fair, but some of the cadmium percentages were markedly low. The lowest result obtained was 35.36 per cent. It is not at all probable that this can be the 2 : 1 salt—Cd 32.3 per cent—for it was noted that the analyses made under the best conditions gave higher results for the metal than in the other cases. From a solution made up in the proportion 4 : 1, the amine hydrochloride being in excess, a crop of crystals which seemed to be homogeneous was obtained. These, on analysis, gave perfectly satisfactory results. The maximum and minimum results in the analysis of this double halide obtained from different sources are recorded below.

I. 0.1430 gram salt gave 0.0578 gram CdO.
0.0655 gram salt gave 0.1073 gram AgCl.
II. 0.4003 gram salt gave 0.1667 gram CdO.
0.1477 gram salt gave 0.2437 gram AgCl.

	Calculated for $[NH_3(CH_3)]_3Cd_2Cl_7$.	Found. I.	II.
Cd	36.70	35.36	36.43
Cl	40.62	40.45	40.75

Double Bromides.

1 : 1 Dimethylamine Bromcadmiate.—When solutions of dimethylamine hydrobromide were mixed with equal, and with larger, molecular quantities of cadmium bromide, and the resulting solutions were allowed to evaporate spontaneously, in some instances crystals in the form of fine white needles appeared. Under other conditions long, thin, striated prisms were obtained. The analyses would indicate that they were the same salt, though the needles contained as much as 2 per cent more cadmium. By diluting and allowing the solution to evaporate very slowly, it was usually possible to get out the larger crystals, which, owing to their compact form, could be better freed from mother-liquors and dried. If the first crop of crystals is allowed to remain in the solution 1 : 4, and the solution is still further concentrated, thick, short, transparent, octahedral grains, seven mm. across, appear mixed with the

flattened, lath-shaped crystals of the 1 : 1 type. A discussion of these will be taken up later.

From the solutions made up in the ratios 1 : 1 and 1 : 2, only the 1 : 1 double bromide was obtained.

I. 0.2603 gram salt gave 0.0857 gram CdO.
0.1124 gram salt gave 0.1602 gram AgBr.
II. 0.3768 gram salt gave 0.1225 gram CdO.

	Calculated for $[NH_3(CH_3)_2]CdBr_3$.	Found. I.	II.
Cd	28.20	28.80	28.44
Br	60.21	60.56	....

2 : 1 Dimethylamine Bromcadmiate.—In all cases where the hydrobromide of the amine was in excess, tabular crystalline masses with projecting rhombohedral prisms were obtained. The solutions were concentrated until they were of a syrupy consistency before any crystals appeared. Several crops from the different beakers were drained and dried and the whole recrystallized from water solution, acidulated with hydrobromic acid. The recrystallized specimens in all cases gave sharp results.

I. 0.2438 gram salt gave 0.0604 gram CdO.
0.1419 gram salt gave 0.2037 gram AgBr.
II. 0.3122 gram salt gave 0.0765 gram CdO.
0.1113 gram salt gave 0.1602 gram AgBr.

	Calculated for $[NH_3(CH_3)_2]_2CdBr_4$.	Found. I.	II.
Cd	21.42	21.67	21.44
Br	60.96	61.00	61.17

1 : 4 Dimethylamine Bromcadmiate.—When solutions in which the hydrobromide of the base bears the ratios 1 : 4, 1 : 5, etc., to the cadmium bromide, were allowed to evaporate spontaneously, there first appeared a crop of long striated, prismatic crystals, which proved on analysis to be the 1 : 1 double bromide. If, without removing these, the solution was still further concentrated, under the crystalline crust, formed as the solution approaches dryness, short, thick, brilliant crystals appeared. These were hard and compact and could be washed by picking them out one by one on a platinum spatula and dipping them momentarily in a beaker of

water. When water was added to the mixture of crystals mentioned above, all quickly dissolved except the short, thick grains. The latter became somewhat opaque, owing to a slight surface decomposition. The analyses were not all concordant, but were fair considering the conditions under which the salt was obtained. The lowest result for cadmium recorded below is from an analysis of a recrystallized specimen of the salt.

I. 0.2458 gram salt gave 0.1051 gram CdO.
0.1640 gram salt gave 0.2279 gram AgBr.
II. 0.2296 gram salt gave 0.0955 gram CdO.

	Calculated for $[NH_3(CH_3)_3]Cd_4Br_9$.	Found. I.	Found. II.
Cd	36.98	37.41	36.39
Br	59.21	59.05	....

Double Iodides.

1 : 1 Dimethylamine Iodocadmiate.—From solutions containing dimethylamine hydroiodide and cadmium iodide in the ratios 1 : 1 and 1 : 2, respectively, tabular, cubical, crystalline masses appeared when the solution had become quite concentrated. The crystals were lifted out, dipped in water, and quickly dried between folds of filter-paper.

When cadmium iodide was in large excess it crystallized out unchanged from the mixed solutions. In the beakers containing the hydroiodide of the amine in excess, crystals appeared only after the solutions had reached a somewhat viscous state. It was found impossible to get them out in a condition approximating purity, so no analyses were made. Alcohol was then tried as a solvent, but with no better results.

0.2938 gram salt gave 0.0703 gram CdO, and 0.3828 gram AgI.

	Calculated for $[NH_3(CH_3)_3]CdI_3$.	Found.
Cd	20.84	20.93
I	70.60	70.35

TRIMETHYLAMINE SALTS.

Double Chlorides.

1 : 1 Trimethylamine Chlorcadmiate.—This salt has already been described and its crystallographic properties investigated by Hiortdahl.[1] It crystallizes from all the mixtures tried, 4 : 1 to 1 : 4, inclusive. When the solutions of the two constituents are rather concentrated, on mixing, the double halide comes down as a white crystalline precipitate. This is sparingly soluble in cold water, easily soluble in warm. From the solution, on standing, beautiful, transparent, monoclinic prisms, several mm. across, appear. These often assume a pseudohexagonal form. Twinning is also quite frequent. The salt crystallizes unchanged from water solution. There were no signs of decomposition when the salt was heated to 270°.

I. 0.4146 gram salt gave 0.1903 gram CdO.
0.3861 gram salt gave 0.5951 gram AgCl.
II. 0.4285 gram salt gave 0.1968 gram CdO.
0.4818 gram salt gave 0.8711 gram AgCl.

	Calculated for $[NH(CH_3)_3]CdCl_3$.	Found. I.	II.
Cd	40.23	40.16	40.18
Cl	38.15	38.07	38.01

3 : 2 Trimethylamine Chlorcadmiate.—After one crop of crystals of the 1 : 1 double chloride above described had been obtained from the solution made up in the ratio 4 : 1 (amine in excess), there appeared, on further concentration, obliquely terminated, flattened prisms. Inasmuch as the formula to which the analyses agreed is an unusual one, it was thought that possibly it might be the 2 : 1 salt, and that the discrepancy in cadmium might arise from impurities. The work was repeated several times, and there seems to be little doubt that the formula below correctly represents the compound. Enough was obtained to admit of a hasty washing with water.

The analyses made, under the most favorable conditions, give a higher percentage for cadmium than in the other cases.

[1] Ztschr. für Kryst., 6, 466; Jahr., 1882, 475.

This would indicate that the impurities tend to lower the percentage of cadmium in the compound, which argues against its being the 2 : 1 salt.

I. 0.1111 gram salt gave 0.0429 gram CdO.
0.1338 gram salt gave 0.2053 gram AgCl.
II. 0.0693 gram salt gave 0.0268 gram CdO.
0.0693 gram salt gave 0.1066 gram AgCl.

	Calculated for $[NH(CH_3)_3]_3Cd_2Cl_7$.	Found. I.	II.
Cd	34.34	33.78	33.88
Cl	37.99	37.90	37.99

Double Bromides.

1 : 1 Trimethylamine Bromcadmiate.—Hiortdahl[1] has described the crystallographic properties of this salt in an article previously referred to. When a mixture of solutions of trimethylamine hydrobromide and cadmium bromide in which the latter is in excess, is concentrated to such an extent that crystals are formed on cooling, a network of long, thin, prismatic crystals separate. These are apparently homogeneous, but no concordant results can be obtained when the crystals are in this form. It is probable that the high percentage for cadmium is to be explained by the fact that the crystals in this form presented a large surface, which prevented the perfect separation of the mother-liquors rich in cadmium bromide. From these same solutions, on slow evaporation, short, thick, skeleton crystals, apparently pseudohexagonal in form, were obtained. The analyses of these were satisfactory in all cases.

I. 0.2627 gram salt gave 0.0819 gram CdO.
0.2071 gram salt gave 0.2825 gram AgBr.
II. 0.1550 gram salt gave 0.0482 gram CdO.

	Calculated for $[NH(CH_3)_3]CdBr_3$.	Found. I.	II.
Cd	27.24	27.27	27.14
Br	58.16	57.97	....

3 : 2 Trimethylamine Bromcadmiate.—When the hydrobromide of the amine was in excess in mixed solutions of cadmium bromide and the former, the above double bromide was

[1] Ztschr. für Kryst., 6, 467; Jahr., 1882, 475.

obtained. The first crops of crystals on analysis gave high results for cadmium, but the successive crops agreed closely with the assigned formula.

The form of the crystals varied widely with the conditions under which they were obtained. Those giving the most concordant results were narrow, flattened, transparent prisms, terminating in pyramidal planes.

The first crops of long, white, striated prisms which gave high results for cadmium, on recrystallization gave fair results. In all cases, when recrystallization was resorted to, the percentage of cadmium was lowered.

I. 0.2680 gram salt gave 0.0716 gram CdO.
II. 0.2384 gram salt gave 0.0639 gram CdO.
0.1243 gram salt gave 0.1702 gram AgBr.
0.5039 gram salt gave 11.56 × 8.104 mgms. $N(CH_3)_3$.

	Calculated for $[NH(CH_3)_3]_3Cd_2Br_7$.	Found. I.	II.
Cd	23.28	23.32	23.45
Br	58.00	58.17	....
$N(CH_3)_3$	18.40	18.58	....

Double Iodides.

1 : 1 Trimethylamine Iodocadmiate.—This salt crystallizes in splendid large cubical masses, resembling potassium iodide in general appearance. From some of the beakers only individual transparent cubes were obtained. These presented a remarkable play of colors in the sunlight. The solutions from which this salt crystallized were made up in the ratios 1 : 1, 1 : 2, 1 : 3, etc.; *i. e.*, cadmium iodide in equal and in larger molecular quantities.

I. 0.2055 gram salt gave 0.0480 gram CdO.
II. 0.4505 gram salt gave 0.1028 gram CdO.
0.1141 gram salt gave 0.1458 gram AgI.

	Calculated for $[NH(CH_3)_3]CdI_3$.	Found. I.	II.
Cd	20.30	20.43	19.97
I	68.81	....	69.00

2 : 1 Trimethylamine Iodocadmiate.—When the molecular ratios of the two halides, trimethylamine hydroiodide and cadmium iodide, stand to each other 2 : 1, 3 : 1, etc., in solu-

tion, and the mixture is allowed to evaporate slowly, very beautiful transparent crystals appear. These are usually modified rhombic prisms. The crystals separated out as individuals in every case. In some instances the 1 : 1 and 2 : 1 double iodides crystallized out side by side in the same beaker. But the difference in crystal form made it easy to effect a separation by mechanical means.

Both of the latter salts are much less soluble in water than the above-described trimethylamine double bromides.

I. 0.3689 gram salt gave 0.0643 gram CdO.
II. 0.3022 gram salt gave 0.0524 gram CdO.
0.1140 gram salt gave 0.1451 gram AgI.

	Calculated for $[NH(CH_3)_3]_2CdI_4$.	Found. I.	II.
Cd	15.17	15.25	15.13
I	68.56	68.72	....

TETRAMETHYLAMMONIUM SALTS.

Double Chlorides.

1 : 1 Tetramethylammonium Chlorcadmiate.—This double salt crystallized in magnificent hexagonal prisms several cm. long. It was obtained from every mixture of the constituent halides experimented with. When the mixed solutions were concentrated to such an extent that crystals were formed on cooling, the results obtained on analysis were not sharp. The slender white columnar crystals formed under such circumstances seemed to hold the mother-liquors with great persistence. On recrystallization the percentage for cadmium accorded with the assigned formula below. The double salt in the form of the hexagonal prisms above mentioned always gave sharp results. This compound crystallized from water unchanged.

Inasmuch as there are double bromides and double iodides formed in the ratio 2 : 1, it was thought that an analogue might be obtained in this series; but there was no evidence of a salt of this composition. From a solution containing mixtures of the two chlorides in the proportion 4 : 1, the ammonium salt in excess, four successive crops of the 1 : 1 compound were obtained before evaporation had proceeded to such

an extent that nothing definite could be further isolated from the mother-liquor.

I. 0.4074 gram salt gave 0.1780 gram CdO.
0.1613 gram salt gave 0.2361 gram AgCl.
II. 0.2054 gram salt gave 0.0893 gram CdO.

	Calculated for $[N(CH_3)_4]CdCl_3$.	Found. I.	II.
Cd	38.29	38.23	38.04
Cl	36.32	36.15	....

Crystallography.[1]

Hexagonal.

$P : P = 142° 15'$
$P : \infty P = 130° 21'$
$\infty P : \infty P = 120°$
Axis $c' = 0.734872$

Double Bromides.

1 : 1 Tetramethylammonium Bromcadmiate.—When concentrated water solutions of cadmium bromide and tetramethylammonium bromide were mixed in the cold in any of the ratios 4 : 1 – 1 : 4, inclusive, a white crystalline precipitate was formed. The precipitates thus formed were redissolved and the solutions diluted. On slow evaporation large, transparent, hexagonal prisms terminating in pyramidal faces were obtained. These very much resemble the double chloride last described. This salt was readily obtained quite pure. The analyses in all instances were consistent with each other and corresponded to the calculated value below.

I. 0.3637 gram salt gave 0.1094 gram CdO.
0.2452 gram salt gave 0.3240 gram AgBr.
II. 0.1822 gram salt gave 0.0547 gram CdO.

	Calculated for $[N(CH_3)_4]CdBr_3$.	Found. I.	II.
Cd	26.34	26.31	26.26
Br	56.24	56.15	....

2 : 1 Tetramethylammonium Bromcadmiate.—From mixed solutions of the two bromides in which tetramethylammo-

[1] I am indebted to Dr. F. P. King, of the Department of Mineralogy, for the crystallographic work. I would take this occasion to express my thanks.

nium bromide was in excess several crops of the 1 : 1 double bromide were first obtained, but finally short, inperfect, flattened rhombic prisms appeared after the solutions had been further concentrated. Mechanical separation had to be used in some cases.

When the crystals were homogeneous, the analyses were always close for the formula assigned.

I. 0.2777 gram salt gave 0.0612 gram CdO.
0.1822 gram salt gave 0.2359 gram AgBr.
II. 0.1575 gram salt gave 0.0349 gram CdO.

	Calculated for $[N(CH_3)_4]_2CdBr_4$.	Found. I.	II.
Cd	19.35	19.28	19.38
Br	55.08	55.02	....

Double Iodides.

1 : 1 Tetramethylammonium Iodocadmiate.—Like the analogous double bromide of tetramethylammonium, this salt is sparingly soluble in cold water. From dilute solutions of the two iodides, in which cadmium iodide was in excess, a white coating of individual crystalline grains appeared on the sides and the bottom of the beakers containing the mixture. The crystal form of the grains, some of which were of microscopic size, was rather indefinite. The mother-liquor, poured off the crystals, deposited, on standing a short time, another crop of the same crystals.

In some of the succeeding crops of crystals, the characteristic double iodide 2 : 1 described below was noticed.

No evidence of a double salt having a higher proportion of cadmium iodide was obtained. From a solution containing 0.625 gram of tetramethylammonium iodide and 15 grams of cadmium iodide only the 1 : 1 double iodide came down on slow evaporation.

I. 0.2981 gram salt gave 0.0665 gram CdO.
0.1786 gram salt gave 0.2213 gram AgI.
II. 0.2467 gram salt gave 0.0559 gram CdO.

	Calculated for $[N(CH_3)_4]CdI_3$.	Found. I.	II.
Cd	19.80	19.51	19.82
I	67.10	66.91	....

2 : 1 Tetramethylammonium Iodocadmiate.—The crystals of this salt usually appeared as white, feathery, individual crystals terminating in a very acute angle. These covered the walls and the bottom of the beaker as a crystalline coating. When the first crop had separated out and the mother-liquor had been allowed to evaporate spontaneously, tabular, transparent crystals, several mm. broad, were formed. These were imperfect, but their general outline seemed to indicate that they were modified tetrahedra. Both this salt and the one last described were very brilliant, and exhibited a remarkable play of colors in the sunlight. The beakers from which the compound was obtained contained an excess of tetramethylammonium iodide. In some cases the two double halides, 1 : 1 and 2 : 1, were noticed in the same beaker. The crystals were too small to be separated conveniently by mechanical means, but the crystal forms were easily recognizable.

I. 0.4543 gram salt gave 0.0762 gram CdO.
0.3559 gram salt gave 0.4348 gram AgI.
II. 0.2866 gram salt gave 0.0476 gram CdO.

	Calculated for $[N(CH_3)_4]_2CdI_4$.	Found. I.	II.
Cd	14.62	14.67	14.53
I	66.05	65.94	....

Conclusions.

1. All the double halides of the alkali metals and ammonium with cadmium, described in the literature, may be classified under the types 1 : 1, 2 : 1, 3 : 1, 4 : 1.

Among the double halides described in this paper, the types met with are 1 : 2, 2 : 1, 3 : 2, 1 : 2, 1 : 4.

Of these it will be noted that the last three types have no analogues among the double halides of the alkali metals and ammonium with cadmium.

2. No double halides corresponding to $(NH_4)_4CdCl_6$ and $(NH_4)_4CdBr_6$., *i. e.* the 4 : 1 type, were obtained.

3. Of the 21 compounds described in this paper, 18 conform to Remsen's law. Three fall under the extension of the law.

SOME DOUBLE HALIDES OF TIN WITH THE ALIPHATIC AMINES AND WITH TETRAMETHYLAMMONIUM.[1]

By C. G. Cook.

The work of Slagle,[2] on the double halides of tin with substituted ammonia compounds, has been extended in this investigation to the compounds formed with the aliphatic amines and with tetramethylammonium.

Preparation of Material.

Amines.—The bases were obtained from the salts furnished by Bender and Hobein.

Tetramethylammonium hydroxide was prepared from its salts by treatment with moist silver oxide according to Hofmann's method[3] and the required salt obtained by neutralizing with the corresponding acid.

Stannous chloride and bromide were made by dissolving the metal in hydrochloric and hydrobromic acids.

The stannic chloride used had been previously prepared by passing chlorine over tin, and was purified by distillation from tin.

Stannic bromide was obtained by the action of bromine on tin. The bromine was allowed to fall, drop by drop, on granulated tin contained in a retort. The reaction, which required but a gentle heat for its initiation, was very violent and continued so long as bromine was added. The product mixed with excess of bromine, distilled over into the receiver and after being purified by fractional distillation was a liquid of light-yellow color which, on cooling, solidified in beautiful white crystals.

Methods of Analysis.

Tin in chlorstannites was determined by dissolving in a solution of ferric chloride in hydrochloric acid, heating to boiling,

[1] From the author's dissertation, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1898. The work was undertaken at the suggestion of Professor Remsen and carried out under his guidance.

[2] This JOURNAL, **20**, 633.

[3] J. Chem. Soc., **4**, 307.

diluting with water, cooling, and titrating the ferrous chloride (formed by the reduction of the ferric chloride) with a standard solution of potassium permanganate.

Stannic tin was determined by reducing to the metallic state with zinc and hydrochloric acid and treating the reduced metal as above. In a few cases tin was estimated as the oxide by evaporating the salt in a weighed crucible with nitric acid and incinerating the base according to the method of Carnelly and O'Shea[1] for determination of tin in stannic bromide, but the method was not found satisfactory.

Amines were estimated by decomposing the salts with sodium or potassium hydroxide and distilling with the aid of steam. The distillate was collected in a known quantity of standard acid and the excess of acid titrated with standard potassium hydroxide solution. For the distillation, a gang-still, composed of four block-tin coils cooled in a water-tank, was used. The method was found both exact and rapid.

The tin of bromstannites was determined by reduction as in the case of stannic salts, since the hydrobromic acid prevented the use of the method applied to chlorstannites.

Preparation of Double Salts.

Concentrated solutions of the two salts were mixed in small beakers in various molecular proportions, as 1 : 1, 1 : 2, 3 : 2, 4 : 1, etc. The mixtures, after being acidulated with the corresponding acids, were evaporated, either by heating or in sulphuric acid and caustic soda desiccators. The successive homogeneous crops of crystals were dried, by pressing between folds of drying-paper, and analyzed.

Compounds Described.

1 : 1 Methylamine chlorstannite.
2 : 1 Methylamine chlorstannate.
1 : 1 Dimethylamine chlorstannite.
2 : 1 Dimethylamine chlorstannate.
1 : 1 Trimethylamine chlorstannite.
2 : 1 Trimethylamine chlorstannate.
1 : 1 Tetramethylammonium chlorstannite.
2 : 1 Tetramethylammonium chlorstannate.

[1] J. Chem. Soc., **33**, 55.

1 : 1 Ethylamine chlorstannite.
2 : 1 Ethylamine chlorstannate.
1 : 1 Triethylamine chlorstannate.
2 : 1 Triethylamine chlorstannate.
3 : 1 Triethylamine chlorstannate.
1 : 1 Methylamine bromstannite.
2 : 1 Methylamine bromstannate.
1 : 1 Dimethylamine bromstannite.
2 : 1 Dimethylamine bromstannate.
2 : 1 Trimethylamine bromstannate.
1 : 1 Ethylamine bromstannite.
2 : 1 Ethylamine bromstannate.
2 : 1 Triethylamine bromstannate.

DOUBLE CHLORIDES.

Methylamine Salts.

1 : 1 Methylamine Chlorstannite, $CH_3NH_3SnCl_3$.—This salt was obtained from a number of mixtures of methylamine hydrochloride and stannous chloride. The crystals were well-defined, transparent, and prismatic in form. Their crystallographic measurements, however, were not made. The salt was much less soluble than stannous chloride, as was shown by the fact that in a few cases the excess of stannous chloride crystallized out in nearly pure condition. Analysis :

	Calculated for $CH_3NH_3SnCl_3$.	Found. I.	II.	III.
NH_3CH_3	12.52	12.51	....	12.48
Sn	46.01	45.98	45.99	....

2 : 1 Methylamine Chlorstannate, $[CH_3NH_3]_2SnCl_4$.—Several mixtures of methylamine hydrochloride and stannous chloride became oxidized by the air, and crystals were formed which proved, on analysis, to be 2 : 1 methylamine chlorstannate. This salt had been described by Hiortdahl.[1] In one case a small crop of white pellets mixed with other crystals was formed. These were separated mechanically, and as a determination of the base seemed to indicate a 1 : 1 stannic salt, an extensive investigation was undertaken to obtain this salt in sufficient quantity for complete anlaysis.

[1] Ztschr. für Kryst., 6, 462.

For this purpose a series of mixtures of methylamine hydrochloride and stannic chloride were made, and the successive crops of crystals analyzed, but all analyses indicated the 2 : 1 salt only. The crystals seemed to be of two forms: the one form, hexagonal rhombohedral, as described by Hiortdahl, the other, transparent scales.

	Calculated for $[CH_3NH_3]_2SnCl_6$.	Found. I.	II.	III.
CH_3NH_2	16.23	16.20	16.25	....
Sn	29.86	30.03	....	30.16

Dimethylamine Salts.

1 : 1 Dimethylamine Chlorstannite, $(CH_3)_2NH_2SnCl_3$.—When concentrated solutions of dimethylamine hydrochloride and stannous chloride were mixed, this salt formed in needle-like crystals. In some cases the crystals seemed to be rhombic, but none could be obtained suitable for crystallographic work. In two beakers the excess of stannous chloride crystallized out in nearly pure condition, showing the difference in solubility of the two salts.

	Calculated for $(CH_3)_2NH_2SnCl_3$.	Found. I.	II.	III.
$(CH_3)_2NH_2$	17.04	17.11	....	17.06
Sn	43.61	....	43.64	43.65

2 : 1 Dimethylamine Chlorstannate, $[(CH_3)_2NH_2]_2SnCl_6$.—A number of mixtures of dimethylamine hydrochloride and stannous chloride, made for the purpose of obtaining chlorstannites, became oxidized. In these, crops of transparent crystals formed. These, on analysis, proved to be the 2 : 1 dimethylamine salt described by Hiortdahl.[1]

Further work showed that this salt crystallized from all mixtures of dimethylamine hydrochloride and stannic chloride on concentration. The salt formed four-sided tables generally. Analysis:

	Calculated for $[(CH_3)_2NH_2]_2SnCl_6$.	Found. I.	II.	III.	IV.
$(CH_3)_2NH_2$	21.79	21.7	21.8	....	....
Sn	27.88	...	...	27.81	27.71

[1] Ztschr. für Kryst., 6, 464.

Trimethylamine Salts.

1 : 1 Trimethylamine Chlorstannite, $(CH_3)_3NHSnCl_3$.—This salt is difficultly soluble and comes down almost quantitatively as a white precipitate from mixtures of concentrated solutions of its constituents. From more dilute solutions, however, crystals in the form of triangular plates were formed. No specimens were obtained suitable for crystallographic work. A large number of determinations of base and tin were made, many of which indicated the 1 : 1 salt.

	Calculated for $(CH_3)_3NHSnCl_3$.	Found. I.	II.	III.	IV.
$(CH_3)_3NH$	21.13	21.07	....	21.09	....
Sn	41.46	....	41.57	....	41.58

2 : 1 Trimethylamine Chlorstannate, $[(CH_3)_3NH]_2SnCl_6$.—This salt was obtained from a number of mixtures of trimethylamine hydrochloride and stannous chloride which were oxidized by the air. The salt had been previously made by Hiortdahl.[1] The crystals were well formed and often of quite good size. Their form is a combination of the cube and octahedron.

	Calculated for $[(CH_3)_3NH]_2SnCl_6$	Found. I.	II.	III.
$(CH_3)_3NH$	26.66	26.51	....	26.81
Sn	26.15	....	25.72	....

Tetramethylammonium Salts.

1 : 1 Tetramethylammonium Chlorstannite, $(CH_3)_4NSnCl_3$.—This salt is formed in all mixtures of the chloride of the base with stannous chloride. The salt was precipitated from moderately concentrated solutions in the form of a crystalline powder, which was dried with difficulty by pressing between folds of drying-paper. In more dilute solutions the crystals took the form of needles. Those solutions which contained an excess of the chloride of the base were easily oxidized during evaporation.

	Calculated for $N(CH_3)_4SnCl_3$.	Found. I.	II.
Sn	39.51	39.59	39.37

[1] Ztschr. für Kryst., **6**, 466.

2 : 1 Tetramethylammonium Chlorstannate, $[N(CH_3)_4]_2SnCl_6$.—When moderately concentrated solutions of stannic chloride and tetramethylammonium chloride were mixed in any proportion a salt was formed which was shown by analysis to have the above formula. The crystals were generally small and not easily soluble in hot, dilute hydrochloric acid. From this solution the salt recrystallized, on cooling, in beautiful, brilliant crystals, which were a combination of the cube and octahedron. Analysis :

	Calculated for $[N(CH_3)_4]_2SnCl_6$.	Found. I.	II.	III.
Sn	24.62	24.3	24.35	....
Cl	44.43	...	....	44.21

Specimens suitable for crystallographic measurements were obtained and the results will be given in a future publication.

Ethylamine Salts.

1 : 1 Ethylamine Chlorstannite, $NH_3C_2H_5SnCl_3$.—This salt was easily formed when concentrated solutions of the hydrochloride of the base and stannous chloride were mixed in various proportions. If the solutions were not too concentrated, the salt formed in white needles soluble in dilute acid. Quite dilute solutions generally became oxidized during evaporation and gave crops of crystals mixed with a stannic salt or composed entirely of the stannic salt. No specimens could be obtained suitable for crystallographic work. Analysis showed the salt to be isomeric with the 1 : 1 dimethylamine chlorstannite.

	Calculated for $C_2H_5NH_3SnCl_3$.	Found. I.	II.	III.
$C_2H_5NH_3$	17.04	17.09	16.99	....
Sn	43.61	43.52	....	43.61

2 : 1 Ethylamine Chlorstannate, $[C_2H_5NH_3]_2SnCl_6$.—The crystals obtained from the oxidized solutions of ethylamine hydrochloride and stannous chloride, mentioned above, as well as from a number of mixtures of stannic chloride and the hydrochloride of the base in various proportions, were found, on analysis, to be the same salt—the 2 : 1 ethylamine chlorstannate. This is isomeric with the 2 : 1 dimethylamine

chlorstannate and, like it, crystallizes well. The crystals are made up of combinations of pyramidal and prismatic faces, in some cases the prismatic form occurring to the exclusion of the pyramids, while in others the latter predominate, giving the crystals an entirely different appearance. The crystals are tough, translucent, and with but little luster.

	Calculated for $[C_5H_5NH_3]_2SnCl_6$.	Found. I.		II.	III.
$C_5H_5NH_3$	21.79	....		21.82	21.75
Sn	27.88	27.58	27.52	....	....

Triethylamine Salts.

When triethylamine hydrochloride and stannous chloride were mixed in concentrated solution there was no evidence of the formation of a double salt, and all attempts to concentrate the solution sufficiently for crystallization to take place only led to the oxidation of the tin salt, and the formation of chlorstannates. To prevent this oxidation, an attempt was made to keep the beakers containing the solutions in an atmosphere of carbon dioxide for some weeks, but evaporation was so slow that sufficient oxygen from the air found its way into the solutions to produce oxidation, and chlorstannates were again formed. The crystals formed by the oxidation of all the above-mentioned mixtures, as well as those from mixtures of triethylamine hydrochloride and stannic chloride were, in general, in the form of rhombic plates, joined by their corners into masses. In some cases the individual crystals showed a tendency to curl up, giving the cluster something of the appearance of a rose. A few large, well-formed crystals were obtained, which much resembled Iceland spar.

About 24 determinations of base were made in the various specimens of crystals, with the most discordant results, and crystals of apparently the same form proved, on analysis, to be mixtures of salts with from 1 to 3 molecules of base. In a few samples which proved to be nearly pure 2 : 1 triethylamine chlorstannate the tin and base were determined with reasonably good results, as follows :

	Calculated for $[(C_2H_5)_2NH]_2SnCl_6$.	Found. I.	II.	III.
$(C_2H_5)_2NH$	38.20	38.20	38.35	37.78
Sn	22.03	21.96	....	22.07

In a number of cases the figures for the base were in the neighborhood of those required by the 1 : 1 salt:

	Calculated for $(C_2H_5)_2NHSnCl_6$.	Found. I.	II.	III.
$(C_2H_5)_2NH$	25.71	26.94	26.17	26.19

Quite a number of the base determinations ran above the per cent required for the 2 : 1 salt, and a few approached the value of the 3 : 1 salt:

	Calculated for $[(C_2H_5)_2NH]_3SnCl_7$.	Found. I.	II.
Base	45.57	44.75	43.85

In almost all cases the crystals had the appearance of those of a pure salt, and in nearly all cases analysis showed them to be mixtures.

DOUBLE BROMIDES.

The preparation of the bromstannites was found to be accompanied with much more difficulty than that of the corresponding chlorine salts. Not only did the solutions oxidize so easily on standing that successive crops of crystals could not be obtained, but also the crystals when removed from the mother-liquor were dried with more difficulty, and in a few cases became oxidized after they had been dried by being pressed between numerous folds of drying-paper. For these and other reasons, the preparation of a few of the possible salts was abandoned. The crystals were generally small and of forms difficult to determine.

The bromstannates, on the other hand, are generally beautifully crystallized, and a number of specimens suitable for crystallographic work were obtained.

Methylamine Salts.

1 : 1 Methylamine Bromstannite, $CH_3NH_3SnBr_3$.—When quite concentrated solutions of methylamine hydrobromide and stannous bromide were mixed the solution remained clear for a moment and then a bright red precipitate was formed in

large quantity. This precipitate dissolved to a colorless, or nearly colorless, solution on the addition of water. From more dilute solutions the salt made its appearance in the form of dark-red, shining scales.

A dilute solution was concentrated by heating, and, on cooling, red needles appeared, arranged in the form of cubes with beautifully fringed edges. These crystals, after standing some days in the mother-liquor, were subjected to the method for determining bases and found to contain a considerable quantity of a bromstannate. Other crystals, which were allowed to stand under similar circumstances, disappeared and a yellow bromstannate took their place. Crystals which were carefully dried soon after precipitation were analyzed and the following results obtained :

	Calculated for $CH_3NH_3SnBr_3$.	Found. I.	II.	III.	IV.
CH_3NH_3	8.22	8.28	....	8.27	....
Sn	30.25	...	30.36	...	29.95

2 : 1 Methylamine Bromstannate, $[CH_3NH_3]_2SnBr_4$.—The crystals of this salt were generally small and not well defined. They formed slowly when mixtures of their constituents were allowed to evaporate spontaneously. Their shape and appearance were quite variable, but analysis showed them to be generally nearly pure. The most common form was that of yellow pellets composed of gummy crystal masses. In a number of cases yellow hexagonal plates were noticed. At other times the salt formed as scales, a few of which were so thin as to appear iridescent.

Among the analyses were the following :

	Calculated for $[CH_3NH_3]_2SnBr_6$.	Found. I.	II.	III.	IV.
CH_3NH_3	9.69	9.63	....	9.70	....
Sn	17.82	...	18.00	...	18.20

Dimethylamine Salts.

1 : 1 Dimethylamine Bromstannite, $(CH_3)_2NH_2SnBr_3$.—This salt was made from a number of mixtures of dimethylamine hydrobromide and stannous bromide, as a crystalline precipitate in the form of beautiful, brilliant, white scales or feathers. Several times it came down with a light-yellow or

brown tint, probably due to impurity in the form of a bromstannate.

	Calculated for $(CH_3)_2NH_2SnBr_4$.	Found. I.	II.	III.
$(CH_3)_2NH_2$	11.41	11.21	11.21	....
Sn	29.20	....	....	28.93

2 : 1 Dimethylamine Bromstannate, $[(CH_3)_2NH_2]_2SnBr_4$.—This salt was made in the usual way by mixing its constituents in a number of proportions and allowing the mixtures to evaporate spontaneously. The crystals, which formed readily and in good size, were brilliant, transparent, hexagonal prisms with modified ends. Analysis :

	Calculated for $[(CH_3)_2NH_2]_2SnBr_4$.	I	Found. II.	III.
$(CH_3)_2NH_2$	13.11	13.14	....	13.14
Sn	17.14	16.76	16.94	....

Trimethylamine Salts.

The hydrobromide of the base was mixed with stannous bromide in a number of proportions, and one crop of white, feather-like crystals and needles was obtained from one beaker, but the solutions showed such a tendency to become oxidized that further efforts to obtain the salt were abandoned.

2 : 1 Trimethylamine Bromstannate, $[(CH_3)_3NH]_2SnBr_4$.—The crystals of this salt were generally small, but under the glass seemed to resemble those of trimethylamine chlorstannate and were probably a combination of cube and octahedron. They were nearly transparent and of a yellow color. Analysis :

	Calculated for $[(CH_3)_3NH]_2SnBr_4$.	I.	Found. II.	III.
$(CH_3)_3NH$	16.75	16.39	....	....
Sn	16.43	....	16.59	16.67

Ethylamine Salts.

1 : 1 Ethylamine Bromstannite, $C_2H_5NH_2SnBr_2$.—Owing to the ease with which the solutions of this salt became oxidized, a large number of crops of the crystals were not obtained, but analysis clearly established their composition to be isomeric with the 1 : 1 dimethylamine bromstannite mentioned above.

The crystals were yellowish-white, shining, semi-transparent, and needle-like in form.

	Calculated for $C_2H_8NH_3SnBr_3$.	Found. I.		II.	
$C_2H_5NH_3$	11.41	....	....	11.48	11.48
Sn	29.2	29.05	29.46	....	....

2 : 1 Ethylamine Bromstannate, $[C_2H_5NH_3]_2SnBr_4$.—The forms of the crystals of this salt were much like those of the corresponding chlorine salt, but in other characteristics the crystals showed more resemblance to the isomeric 2 : 1 dimethylamine bromstannate. They were lustrous, of a bright-yellow color, and nearly transparent. In most cases the prismatic faces, and also the pyramidal ones, were developed, but some crystals on which the pyramidal form predominated were noticed.

	Calculated for $[C_2H_5NH_3]_2SnBr_6$.	Found. I.	II.	III.
$C_2H_5NH_3$	13.11	13.26	....	13.37
Sn	17.14	....	17.15	....

Triethylamine Salts.

When triethylamine hydrobromide was mixed with stannous bromide, beautiful, white, lustrous fibers were formed. The crystals were removed from several beakers and dried with difficulty by pressing between folds of drying-paper. After these crystals were dry, or nearly so, they became bright-yellow. This was supposed to be due to oxidation, and further work with this salt was abandoned.

2 : 1 Triethylamine Bromstannate, $[(C_2H_5)_3NH_2]_2SnBr_4$.—This salt was obtained in the usual manner, but no specimens of crystals suitable for measurement were obtained. In general, the form was that of rhombic plates, somewhat resembling those of the corresponding chlorine salt; they were yellow in color, and in some cases transparent. The percentage of base was in a number of analyses a little high, but there was no evidence of the formation of other salts as in the case of the triethylamine chlorine salts. Analysis:

	Calculated for $[(C_2H_5)_3NH]_2SnBr_6$.	Found. I.	II.	
$(C_2H_5)_3NH$	25.49	....	25.53	25.53
Sn	14.70	14.77	....	....

Conclusions.

A marked regularity is found throughout this whole series of salts. All of them, with one exception, belong to the 1 : 1 or 2 : 1 form, and all obey Remsen's law as first stated. The chlorine and bromine salts show many crystallographic resemblances, though their colors are often different.

The salts containing tin in the stannous condition seem to show differences in the ease with which they are oxidized, but so many modifying influences come in that no generalizations can be made.

NOTES ON THE DOUBLE HALIDES OF TIN WITH THE ORGANIC BASES.

By George M. Richardson and Maxwell Adams.

Practically all of our work upon the double chlorides of tin with aniline and the toluidines has been anticipated by the work of Slagle,[1] and was discontinued upon learning of his work upon these compounds.

Although our work, for the most part, confirms the results given by Slagle, we have, however, obtained some compounds not described by him, and it seems that a brief description of these may not be out of place.

Aniline Compound.

Tetraniline Chlorstannate, $(C_6H_5NH_2)_4SnCl_6$.—This compound was obtained by mixing 300 cc. of a normal aniline hydrochloride solution with 50 cc. of a normal stannous chloride solution. This mixture, on standing three days, gave a considerable yield of the dianiline chlorostannite,

$$(C_6H_5NH_2)_2SnCl_4,$$

but the mother-liquor from these crystals, after standing three weeks, gave a crop of clear, well-formed crystals, which gave upon analysis :

	Calculated for $(C_6H_5NH_2)_4SnCl_6$.	Found. A.	B.
Sn	15.16	14.91	14.98
Cl	36.50	36.48	36.37

[1] This Journal, **20**, 633.

The mother-liquor from these crystals after standing two months more, gave still another crop of crystals, evidently like the previous ones, which gave on analysis :

	Found. A.	B.
Sn	14.97	14.94
Cl	36.18	36.13

These crystals are well formed and the salt is comparatively stable.

Dimethylaniline Salts.

Working with dimethylaniline we have obtained only the dimethylaniline chlorostannite.

Dimethylaniline Chlorostannite, $C_6H_5NH(CH_3)_2SnCl_3.\frac{1}{2}H_2O$. —While this salt was evidently the one most readily formed, we have no reason to believe that others could not be obtained. This compound was, in its preparation and crystalline form, strictly analogous to the corresponding toluidine compounds described by Slagle.[1]

The salt gave upon analysis :

	Calculated for $C_6H_5NH(CH_3)_2SnCl_3.\frac{1}{2}H_2O$.	Found. A.	B.
Sn	33.19	33.09	33.13
Cl	29.96	30.40	30.49
H_2O	2.53	2.65	....

Double Bromides of Aniline and Tin.

Three distinct salts of aniline hydrobromide and tin bromide have been prepared and analyzed ; they are :

Aniline bromostannite, $C_6H_5NH_3SnBr_5$,
Dianiline bromostannate, $(C_6H_5NH_3)_2SnBr_6$, and
Tetraniline bromostannate, $(C_6H_5NH_3)_4SnBr_8$.

Aniline Bromostannite, $C_6H_5NH_3SnBr_5$.—This salt was prepared by mixing hot solutions of aniline hydrobromide and stannous bromide in molecular proportions, and allowing the mixture to stand for six or twelve hours.

The crystals were small but well defined, with a spear-like form, being white at first but changing to a yellow color upon standing. The crystals melted at 152° and were solu-

[1] This JOURNAL, **20**, 640.

ble in water, the solution rapidly becoming turbid. They were also soluble in alcohol, ether, and chloroform, but any attempt to recrystallize the salt from these solvents resulted in the oxidation of the tin to the stannic condition.

Analysis of this salt gave :

	Calculated for $C_6H_5NH_3SnBr_3$.	Found. A.	Found. B.
Sn	26.28	26.19	52.56
Br	52.93	26.06	52.85

All efforts to prepare other double bromides containing stannous tin, from solutions of varying proportions, were unsuccessful. The salt $C_6H_5NH_3SnBr_3$ was always formed or else the tin was oxidized to the stannic condition, oxidation always taking place when the solution was allowed to stand for any length of time.

Dianiline Bromostannate, $(C_6H_5NH_3)_2SnBr_6$.—This salt was formed by mixing hot solutions of aniline hydrobromide and stannic bromide in the portions of 2 molecules of aniline hydrobromide to 1 of stannic bromide, or with a larger portion of the stannic bromide. It was also formed when a solution of stannous bromide and aniline hydrobromide (when the aniline hydrobromide is not in excess of the proportions given above) was allowed to stand. It formed flat, tabular, straw-colored crystals. It was soluble in water, forming a milky precipitate upon standing for any length of time. The salt was readily soluble in alcohol, and less soluble in ether and chloroform. It began to sublime, with decomposition, at 250°.

An analysis of the salt gave :

	Calculated for $(C_6H_5NH_3)_2SnBr_6$.	Found. A.	Found. B.
Sn	15.12	15.05	15.11
Br	60.95	60.81	60.92

Tetraniline Bromostannate, $(C_6H_5NH_3)_4SnBr_8$.—This salt was formed by mixing solutions of aniline hydrobromide and stannic bromide in the proportions indicated by the formula, or by allowing solutions of stannous bromide, in which there was an excess of aniline hydrobromide, to stand.

The salt crystallized out in well-formed light-yellow crystals, soluble in alcohol, slightly soluble in ether and in chloro-

form. It was less soluble in water than the dianiline bromostannate, and crystallized out first from a solution containing both salts. It melted with decomposition at 274°.

Analysis of the salt gave:

	Calculated for $(C_6H_8NH_3)_4SnBr_8$.	Found. A.	B.
Sn	10.48	10.35	10.42
Br	56.35	56.39	56.24

STANFORD UNIVERSITY, CAL.,
October 3, 1899.

Contributions from the Chemical Laboratory of Harvard College.

CXVI.—ON THE CONSTITUTION OF α-DIBROMDINITROBENZOL—PARADIBROMORTHODINITROBENZOL.

BY D. F. CALHANE AND P. M. WHEELER.

When paradibrombenzol is treated with a mixture of fuming nitric acid and strong sulphuric acid the product consists of several isomeric dibromdinitrobenzols, some of which have been investigated by Austen,[1] who succeeded in isolating two of them, α-dibromdinitrobenzol, melting at 159°, and β-dibromdinitrobenzol, melting at 99°–100°. After studying[2] several derivatives of the β-compound he established[3] its constitution ($Br1.NO_2 2.Br4.NO_2 6$) by converting it into the parabromdinitrophenol ($OH1.NO_2 2.Br4.NO_2 6$). The α-compound, on the other hand, occurred in so much smaller quantity that he was unable to settle its constitution definitely, although he made progress in this direction by converting it into a paradibromnitraniline by the action of alcoholic ammonia. A replacement, such as this, of one nitro group in a dinitro body by an amino group, does not prove that the two nitro groups are in the ortho position to each other, as was supposed by Laubenheimer,[4] since Lobry de Bruyn[5] has shown in a number of papers that such reactions take place easily with paradinitro compounds and also with trinitro bodies of various structure. They prove nothing, therefore, regarding the constitution of the aromatic substances which take part in them,

[1] Ber. d. chem. Ges., **9**, 621. [2] *Ibid.*, 918.
[3] Am. J. Sci. (Silliman's), [3] **16**, 46. [4] Ber. d. chem. Ges., **9**, 1827; **11**, 1155.
[5] Rec. trav. chim. Pays-Bas., **9**, 190, 208, 211 (1890); **13**, 118, 148 (1894).

and the question of the constitution of α-dibromdinitrobenzol must be considered an open one.

The study of the paradibromdinitrobenzols was undertaken in the hope of throwing more light on the replacement of bromine by hydrogen in reactions between bromdinitrobenzols and sodic ethylate, which has been studied now for some years in this laboratory. The present paper has not carried the work further than the preliminary step of establishing the constitution of the α-isomer, but the investigation will be extended to the reactions of this body and the study of the other isomers.

To determine its constitution the α-dibromdinitrobenzol was reduced with a mixture of acetic acid and zinc dust to a dibromphenylenediamine, melting at 94°–95°. The bromine was then removed from this by prolonged treatment with sodium amalgam and water, when a small quantity of orthophenylenediamine was obtained. This result was confirmed by treating the paradibromphenylenediamine with phenanthrenequinone, which gave a paradibromphenanthrophenazine, or paradibromdiphenylenechinoxaline,

$$C_6H_2Br_2N_2C_2(C_6H_4)_2,$$

which melts at 297°; and also by treating it with benzil, from which was obtained the paradibromdiphenylchinoxaline,

$$C_6H_2Br_2N_2C_2(C_6H_5)_2,$$

melting at 215°–216°. As such chinoxalines are formed only from orthodiamines, it follows from all our observations that the two amino groups, and consequently the two nitro groups are in the ortho position to each other; and, as the substance was made from paradibrombenzol, it must be the paradibromorthodinitrobenzol (Br1.$NO_2$2.$NO_2$3.Br4). Our work, therefore, shows that the structure assigned to it by Austen is correct. We may add that the paradibromdiamine seemed also to give with benzaldehyde the characteristic reaction of an orthodiamine, but as the constitution was already sufficiently proved we did not pursue this work further.

The main object of the research—the study of the reaction of the paradibromorthodinitrobenzol must be postponed for the present, as the amount of this isomer formed is so small

that our whole supply was used up in the determination of its constitution. The following preliminary experiments show that it is a reactive substance and that there is promise of interesting derivatives; sodic ethylate acted upon it even in the cold, as shown by the appearance of a deep-red color and the formation of both sodic bromide and sodic nitrite. Sodium malonic ester in the cold also gave a red coloration, and sodic bromide but no nitrite was formed.

EXPERIMENTAL PART.

The α-paradibromdinitrobenzol used in this work was prepared by the method of Austen[1] as follows: 200 grams of paradibrombenzol (made according to Jannasch[2]) were dissolved in 650 grams of fuming nitric acid (sp. gr. 1.505), and mixed with the same volume of strong sulphuric acid. Disregarding the red oil precipitated in this way, the mixture was warmed, when a violent reaction took place, during which the heat was removed. After this had come to an end the liquid was boiled gently for three hours in a flask closed with a porcelain crucible. It was then allowed to cool, and, before the oil had solidified, poured into a large quantity of water contained in an evaporating dish for convenience in removing the solid, which formed after standing over night. The crude product freed from acid by washing with water amounted to 246 grams instead of 275 grams; that is, 90 per cent of the theoretical yield.

In order to separate the isomers the crude product was recrystallized from glacial acetic acid, as recommended by Austen, when we found that the α-isomer could be obtained with but little difficulty by using the proper amount of the solvent. For this purpose 50 grams of the dry mixture were dissolved in 85 cc. of glacial acetic acid, and the solution was allowed to stand over night in a cool place. (The temperature of the laboratory was too high to give a copious crystallization.) From four such solutions, containing 200 grams of the crude product in all, 12.5 grams of crystals were obtained which melted at 152°. These 12.5 grams of substance were dissolved by heat in 50 cc. of glacial acetic acid, and after stand-

[1] Ber. d. chem. Ges., **9**, 621. [2] *Ibid.*, **10**, 1355.

ing for two hours yielded 9.5 grams of crystals melting at 159°, and, therefore, pure α-paradibromdinitrobenzol. From the mother-liquors 2 grams more of pure substance were obtained, making 11.5 grams in all from 200 grams of the crude product, or 5.75 per cent. The amount of the α-isomer formed is, of course, larger than this, as a considerable portion of it must have remained mixed with the β-isomer in the mother-liquors; but our results confirm the observation of Austen that the α-isomer forms but a small part of the product of the reaction. The α-dibromdinitrobenzol forms colorless prisms with a vitreous luster. It was analyzed for greater surety, and gave 48.96 per cent of bromine instead of the 49.08 per cent calculated from the formula.

Reduction of α-Paradibromdinitrobenzol.

One gram of the α-paradibromdinitrobenzol, mixed with 25–30 cc. of acetic acid containing 70 per cent of glacial acetic acid, was treated in a flask with 2 grams of zinc dust, and 2 grams more of zinc dust were added later in small portions with 10–15 cc. more of the acid. During the reduction it was found best to keep the temperature at about 60°–70° by allowing the flask to stand on a steam radiator, but as the dilute acetic acid had only a slight solvent action on the nitro compound, the mixture was heated from time to time more strongly on the water-bath. The action was finished when all the substance had gone into solution, forming a mahogany-brown liquid, which usually took place in from two to three hours. The solution was then allowed to cool, when it deposited large crystals of zincic acetate, which, after standing for some time, were filtered out and washed with more of the acetic acid till white. The dark-colored filtrate was diluted with a large volume of water which threw down the free base as a pinkish-brown gelatinous mass. The liquid with the precipitate suspended in it was then distilled with steam, when in some cases the base came over after a few minutes in a nearly pure state. In other cases it was necessary to distil off about two-thirds of the liquid before any of the amine appeared, but, if then the distillation was interrupted, and the contents of the flask diluted, a heavy precipitate was ob-

tained, and after this the amine distilled over freely. It took usually two hours to drive over the whole of the base. The distillation must not be run too rapidly, as in that case the product was contaminated with a yellow oil, and throughout the process care must be taken to avoid the clogging of the condenser by the solid portion of the distillate. When the distillation ran successfully the amine formed a white gelatinous mass, which, on filtering, shrank very much, and was seen to be a felted collection of slender needles. It was filtered at once, and should be dried by pressing between filter-paper and standing in the desiccator as soon as possible, since it turns brown quickly if left in contact with water. The yield was on the average 0.75 gram from 1 gram instead of 0.82 gram; that is, 92 per cent of the theory. The yield was increased somewhat by dissolving the crystals of zincic acetate, mentioned above, in water, extracting with benzol, and precipitating the chloride of the base from the benzol solution by passing gaseous hydrochloric acid through it; but the amount obtained in this way was so small that it did not pay for the time and labor expended.

As crystallization from hot water partially decomposed the base, as was shown by the appearance of a brown color, and as it was so soluble in the organic solvents that we could not purify it by crystallization from these, the substance was prepared for analysis only by the distillation with steam, as already described. It was dried *in vacuo* and analyzed with the following result:

0.2592 gram of the substance gave, by the method of Carius, 0.3641 gram of argentic bromide.

	Calculated for $C_6H_3Br_3(NH_2)_2$.	Found.
Br	60.15	59.77

The base is, therefore, a dibromphenylenediamine, in which, as is proved later in this paper, the two atoms of bromine are in the para, and the two amino groups in the ortho, position to each other.

Properties of Paradibromorthophenylenediamine, $C_6H_2Br_2(NH_2)_2$.—As obtained by distillation with steam it forms a felted mass of small white needles. By careful crys-

tallization from water it can be obtained sometimes in radiating groups of long white needles, looking like thistle-down. From alcohol it crystallizes in flat groups of short radiating needles. On long exposure to the air it turns light-brown, and this change in color takes place much more rapidly, even in a few hours, if the substance is moist or suspended in water. It melts at 94°–95°, and can be sublimed, but this process is too destructive to be used to advantage in its purification. It distils with steam and is very soluble in alcohol, ether, benzol, acetone, or chloroform; slightly soluble in cold water, more soluble in hot, but crystallization from this solution is almost invariably attended by decomposition, as shown by the appearance of a brown color. It shows weak basic properties. It dissolves easily in glacial acetic acid, and is thrown down apparently unaltered by dilution. Hot strong hydrochloric acid or hydrobromic acid dissolves it, and, on cooling, white needles of the corresponding salt are deposited; but, if the pure salt is needed, it is better to make it by passing the gaseous acid through a solution of the diamine in benzol, as described in the next section. Cold strong nitric acid dissolves it with a deep-red color, and on dilution a purple-red amorphous precipitate was thrown down. It is insoluble in cold, soluble in hot strong sulphuric acid, but this solution deposits nothing on dilution or cooling. Alkalies do not dissolve it, but promote its decomposition. Bromine gives a red oily precipitate with a solution of the diamine in acetic acid. The best way of purifying the paradibromorthophenylenediamine is by careful distillation with steam.

Chloride of Paradibromorthophenylenediamine, $C_6H_2Br_2NH_2NH_2Cl$.—This salt was made by dissolving the free base in anhydrous benzol, and passing dry hydrochloric acid through the solution, when it appeared as a pale-pink, amorphous precipitate. After filtering off the benzol it was purified by one recrystallization from hot concentrated hydrochloric acid, dried by pressing between filter-papers, and analyzed with the following result:

0.1760 gram of the substance gave, by the method of Carius, 0.3036 gram of a mixture of argentic chloride and argentic bromide.

	Calculated for $C_6H_3Br_2NH_2NH_2Cl$.	Found.
Cl and Br	64.63	64.91

Properties.—The salt, as precipitated from a benzol solution of the base with hydrochloric acid, forms a pinkish-white, amorphous powder, but appears in white, sparkling needles when crystallized from concentrated aqueous hydrochloric acid. When heated it decomposes, hydrochloric acid escapes, and the free base sublimes. The same decomposition takes place more slowly at ordinary temperatures. It is insoluble in cold water, and is broken up by hot water into the free base and hydrochloric acid; insoluble in benzol.

Paradibromorthophenylenediacetamide, $C_6H_2Br_2(NHCOCH_3)_2$. —This substance was obtained by heating the paradibrom-orthophenylenediamine for five minutes with acetic anhydride. The clear solution deposited nothing on cooling, but after treatment with water and neutralization with potassic hydrate a heavy white precipitate was formed, which was purified by crystallization from hot alcohol, dried at 150°, and analyzed with the following result:

0.1774 gram of the substance gave, by the method of Carius, 0.1929 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(NHCOCH_3)_2$.	Found.
Br	45.71	46.28

The substance therefore is the diacetyl compound of the diamine, as would be expected from the work of Bistrzycki and Ulffers.[1]

Properties.—It crystallizes from hot alcohol in white, thread-like crystals matted together into a mass. It melts between 265° and 269° with decomposition, and is soluble in hydrochloric acid, alcohol, or glacial acetic acid; insoluble in hot water.

Conversion of α-Paradibromphenylenediamine into Orthophenylenediamine.

The paradibromphenylenediamine, obtained by the reduction of α-paradibromdinitrobenzol, as described above, was suspended in water in a flask and treated with sodium amal-

[1] Ber. d. chem. Ges., **23**, 1876 (1890).

gam at ordinary temperatures in a stream of carbonic dioxide, which served to protect the solution from the air and to convert the sodic hydrate formed into sodic carbonate. After the reaction had gone on for three weeks a portion of the solution was tested with chlorine water and bisulphide of carbon, when a strong test for bromine was obtained. The mixture was then shaken with chloroform, and the chloroform extract yielded, on evaporation, a yellow oil, which was dissolved in hot water. This aqueous solution deposited, on evaporation, white plates, which were free from bromine, dissolved in hydrochloric acid, and melted at 100°. Orthophenylenediamine melts at 102° but, although the amount of our crystals was too small to see if the melting-point could be raised by recrystallization, there can be no doubt that our diamine was the ortho compound. It also gave with a concentrated solution of ferric chloride the characteristic deep-red color. Our inference that this product was orthophenylenediamine was confirmed by the following experiments:

Action of the α-Dibromphenylenediamine with Phenanthrenequinone. Paradibromphenanthrophenazine, or Paradibromdiphenylenechinoxaline.—To study this action 0.2 gram of the diamine were dissolved in alcohol and mixed with somewhat less than the calculated amount of phenanthrenequinone dissolved in hot glacial acetic acid. A flocculent lemon-yellow precipitate was deposited at once, which, after being washed and dried, was purified by crystallization from boiling benzol, dried at 100°, and analyzed with the following results:

I. 0.1993 gram of the substance gave, by the method of Carius, 0.1735 gram of argentic bromide.

II. 0.2783 gram of the substance gave, by the method of Carius, 0.2412 gram of argentic bromide.

	Calculated for $C_{20}H_{10}Br_2N_2$.	Found. I.	Found. II.
Br	36.53	37.03	36.88

These analyses prove that this substance is the expected chinoxaline or azine, $C_6H_2Br_2N_2C_2(C_6H_4)_2$, formed by the removal of two molecules of water from the diamine and the quinone.

Properties of Paradibromphenanthrophenazine or Paradibromdiphenylenechinoxaline.—It crystallizes from benzol in slightly radiating bunches of silky yellow needles. It melts at about 297°, and is practically insoluble in cold, sparingly soluble in hot ethyl or methyl alcohol; insoluble in cold ligroin or acetone, very sparingly soluble in either of these solvents when hot; sparingly soluble in ether or glacial acetic acid; somewhat soluble in benzol or chloroform, especially if hot; insoluble in water. Strong hydrochloric acid, whether cold or hot, gives no apparent action, which is extraordinary, as Hinsberg[1] has found that the phenanthrophenazine gives a deep-red color with all the mineral acids, and the only difference between his compound and ours is that ours contains two atoms of bromine in place of two of hydrogen. This difference in behavior disappears, however, when the action of strong sulphuric acid is studied, as this converts our chinoxaline, even in the cold, into a dark claret-colored soluble substance. Strong nitric acid had no apparent action in the cold, but, if heated with the chinoxaline, dissolved it slowly with a reddish color. Fuming nitric acid dissolved it at once in the cold with a deep, wine-red color, and on dilution a new substance was precipitated. Sodic hydrate, whether cold or boiling, had no apparent effect on the substance. The best solvent for it is boiling benzol, or chloroform, but it is not freely soluble even in the latter.

Action of α-Dibromphenylenediamine with Benzil. Paradibromdiphenylchinoxaline.—To try this action, strong hot alcoholic solutions of the diamine and benzil were mixed in such proportions that there was a little more than 1 molecule of the diamine for each molecule of benzil. The reaction took place less easily than the corresponding one with phenanthrene quinone, for, whereas that acted in the cold, in this case it was necessary to heat in a flask with a return condenser for half to three-quarters of an hour in order to bring the reaction to an end. As the solution cooled the product crystallized out in bunches of white needles, which were so nearly pure that only one crystallization from alcohol and a little benzol was necessary to raise it to its constant melting-point, 215°–

[1] Ann. Chem. (Liebig), 237, 340.

216°. It was then dried at 100° and analyzed with the following result:

0.2187 gram of the substance gave, by the method of Carius, 0.1890 gram of argentic bromide.

	Calculated for $C_{30}H_{18}Br_2N_2$.	Found.
Br	36.36	36.77

The substance is therefore paradibromdiphenylchinoxaline, $C_6H_4Br_2N_2C_4(C_6H_5)_2$.

Properties.—The chinoxaline crystallizes in sheaf-shaped bunches of long, white, somewhat curved and branched, needles, which, when better developed, appear under the microscope, as slender prisms, sometimes terminated by a single plane, sometimes bluntly pointed. It melts at 215°–216°, and is readily soluble in ether, benzol, chloroform, acetone, or carbon disulphide; nearly insoluble in cold ethyl or methyl alcohol, sparingly soluble when they are hot; sparingly soluble in cold ligroin, readily in it when hot; slightly soluble in cold glacial acetic acid, soluble in it when hot. Strong hydrochloric acid has no apparent action on it either hot or cold, whereas the corresponding unsubstituted compound forms a salt with hydrochloric acid. Cold strong sulphuric acid dissolves it easily with a claret-red color. Cold, strong nitric acid also dissolves it with a lemon-yellow color, and fuming nitric acid acts in the same way. Sodic hydrate, whether cold or hot, has no action upon it. The best solvent for it is alcohol mixed with a little benzol.

The research will be continued in this laboratory and extended to the other isomeric dibromdinitrobenzols formed at the same time with the body studied in this paper.

Contributions from the Chemical Laboratory of Cornell University.

PHENYL MUSTARD OIL AS A REAGENT FOR THE DETECTION OF THE ALCOHOLIC HYDROXYL GROUP.

By W. R. Orndorff and F. A. Richmond.

Phenyl isocyanate, $C_6H_5N=C=O$, combines very readily with alcohols, phenols, and oximes to form urethanes, and

with substituted ammonias to give derivatives of urea. Indeed, the fact that it reacts so easily, without the formation of by-products, and that the compounds formed are readily purified and analyzed, makes this substance a very valuable reagent in the organic chemical laboratory for the detection of the groups characteristic of the above-mentioned classes of compounds. Unfortunately, the substance is no longer made on the large scale in the factory and it is not easy to make in any quantity in the laboratory. Its high cost and the difficulty of preparing the substance have therefore prevented its coming into general use. The analogously constituted compound, phenyl mustard oil, $C_6H_5N=C=S$, can be readily made in the laboratory and is a comparatively cheap substance. If it should be found to react as readily as phenyl isocyanate with the classes of organic compounds above enumerated, and could be substituted for this substance, much would therefore be gained. With this idea in view, the following investigation of the action of phenyl mustard oil on alcohols and phenols was undertaken. It was soon found, however, that phenyl mustard oil reacts much less readily than phenyl isocyanate, so that it is highly improbable that it will ever replace this substance as a reagent in the chemical laboratory. With monacid alcohols of the paraffin series, primary, secondary, and tertiary, it reacts to form well-crystallized thiourethanes, but it does not combine with unsaturated alcohols, polyacid alcohols, phenols or alcohols of the benzene series to form similar compounds. It does not combine with acids of the paraffin or the benzene series. Its use as a reagent for the detection of the hydroxyl group is therefore limited to the monacid alcohols of the paraffin series.

The only statements found in the literature regarding the action of phenyl mustard oil on alcohol and phenols are those of A. W. von Hofmann[1] and others[2] describing the product of the action of phenyl mustard oil on ethyl alcohol, of A. E. Dixon[3] and later of H. Lloyd Snape[4] on the action of phenyl mustard oil on phenols, and of Tessmer and Volkmann[5]

[1] Ber. d. chem. Ges., **2**, 120; **3**, 772.
[2] See Lehrbuch der Organischen Chemie, V. Meyer u. P. Jacobson, II, 1, 203.
[3] J. Chem. Soc., **57**, 268.
[4] *Ibid.*, **69**, 98.
[5] Ber. d. chem. Ges., **18**, 972.

on the formation of diphenyl thiourea, $SC\langle^{NHC_6H_5}_{NHC_6H_5}$, when phenyl mustard oil and glycerin are heated together.

Hofmann heated molecular proportions of phenyl mustard oil and absolute alcohol in a sealed tube to a temperature of 110°–115° C. for three hours. The product, on recrystallization from alcohol, consisted of white crystals melting at 65° C. To this product Hofmann assigns the following structural formula :

$$C_6H_5NH\diagdown \atop C_2H_5O\diagup C{=}S.$$

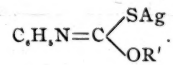
A much simpler method of making this phenyl thiourethane is given in Meyer and Jacobson's Organische Chemie, II, 1, 203. According to these authors it is formed extraordinarily easily by simply boiling phenyl mustard oil with four times its weight of absolute alcohol for several hours.

Dixon heated phenol and phenyl mustard oil in sealed tubes to 140°–150° C., and obtained a product crystallizing in octahedra, which resembled sulphur in appearance and color and melted at 149°–151° C. A determination of the amount of sulphur in this compound gave 13.48 per cent, while the theory for $C_6H_5NH.CS.OC_6H_5$ requires 13.97 per cent of sulphur. Later Snape obtained the same compound by a similar method, but he heated his tubes to a higher temperature and for a longer time, and obtained a larger yield of material. He describes his product as crystallizing from absolute alcohol in yellow leaves or needles melting at 148° C. Like Dixon, he merely determined the amount of sulphur in this compound and found 14.03 per cent. Snape further attempted to effect a combination of phenyl mustard oil with resorcin, hydroquinone, and glycol, but without success.

From the ease with which phenyl mustard oil reacts with ethyl alcohol[1] we expected it would react with all alcohols in a manner analogous to that of phenyl isocyanate forming, instead of urethanes, thiourethanes. These thiourethanes could

[1] These two substances unite when they are mixed and allowed to stand for some time at the room temperature.

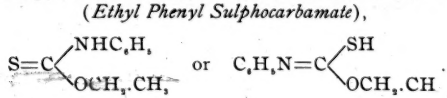
be very readily analyzed by the Kjeldahl method for nitrogen and by the Carius method for sulphur, and if these two determinations checked, the composition of the substance would be determined as accurately as if a complete combustion analysis had been made. These thiourethanes are also acid in their nature and form very readily with an alcoholic, ammoniacal solution of silver oxide, a silver salt, which probably has the following composition :[1]



These silver salts are easily purified and analyzed, and from the amount of silver found it is easy to calculate the composition of the thiourethane, thus doing away with the longer determinations of the amounts of nitrogen and sulphur and simplifying the method very much.

We give below the results of our experiments with the various alcohols and phenols used.

The Compound of Phenyl Mustard Oil with Ethyl Alcohol (Ethyl Phenyl Sulphocarbamate),



This compound, which, as already stated, was first made and described by Hofmann, was prepared as follows : 5 grams of pure phenyl mustard oil, having a constant boiling-point of 222° C., were heated with a slight excess of absolute alcohol in a sealed tube to a temperature of 110°–115° C. for three hours. After cooling, the tube was found to contain a solid substance which, on recrystallization from alcohol, gave beautiful white prisms, melting at 71°–72°. A crystallographic examination of these crystals by Mr. J. E. Gignoux, under the direction of Prof. A. C. Gill, of the mineralogical department of this university, showed their complete identity with the crystals of ethyl phenylsulphocarbamate made by Hofmann and measured by Groth. Later we adopted the method

[1] In this formula R' represents any univalent alcoholic radical like CH_3, C_2H_5, etc.

of preparation given by V. Meyer and P. Jacobson and mentioned above.

From this ethyl phenylsulphocarbamate we made the silver salt according to the method given by Liebermann[1] and analyzed this. The following results were obtained.[2]

I. 0.3242 gram substance gave 0.1216 gram Ag.
II. 0.3847 gram substance gave 0.1446 gram Ag.

	Calculated for $C_6H_5N=C(SAg)(OC_2H_5)$	Found. I.	II.
Ag	37.45	37.50	37.58

The above results show that phenyl mustard oil and ethyl alcohol combine very readily to form ethyl phenylsulphocarbamate. The substance crystallizes very beautifully in the triclinic system, is insoluble in water, soluble in alcohol, ether, chloroform, benzene, acetone, carbon bisulphide, and acetic ether, and melts at 71°–72° C. When heated to its boiling-point it decomposes into phenyl mustard oil and alcohol, forming at the same time both thiocarbanilide (diphenyl thiourea, $S=C(NHC_6H_5)(NHC_6H_5)$), and carbanilide diphenyl urea $O=C(NHC_6H_5)(NHC_6H_5)$), as stated by Hofmann.

The Compound of Phenyl Mustard Oil with Methyl Alcohol (Methyl Phenylsulphocarbamate),

$S=C(NHC_6H_5)(OCH_3)$ or $C_6H_5N=C(SH)(OCH_3)$.

The methods employed in making this compound were similar to those used in making the ethyl compound. On recrystallization from alcohol white crystals were obtained, melting at 97° C., insoluble in water and easily soluble in alcohol, ether, chloroform, acetone, benzene, and acetic ether. Analysis gave the following results :

[1] Ann. Chem. (Liebig), **207**, 142.

[2] The atomic weights used in this paper are those given by F. W. Clarke in the new edition of his "Recalculation of the Atomic Weights" (1897).

Determination of the Amount of Nitrogen (Kjeldahl Method).

I. 0.5159 gram substance gave 0.05256 gram NH_3, corresponding to 0.04329 gram N.

II. 1.3218 gram substance gave 0.13223 gram NH_3, corresponding to 0.1089 gram N.

Determination of the Amount of Sulphur (Carius Method).

I. 0.1268 gram substance gave 0.1775 gram $BaSO_4$.

II. 0.2330 gram substance gave 0.3263 gram $BaSO_4$.

	Calculated for $S=C<^{NHC_6H_5}_{OCH_3}$	Found. I.	Found. II.
N	8.397	8.238	8.39
S	19.175	19.225	19.223

These results show that the compound has the composition of the methyl ester of phenylsulphocarbamic acid, and that methyl alcohol reacts very readily with phenyl mustard oil.

A crystallographic examination of the crystals of this compound by Mr. J. E. Gignoux gave the following results:

Crystal system, triclinic, probably hemihedral (pedial class of Groth).

The crystals are usually thin plates, parallel to the face taken as the basal pinacoid.

From measurements on 31 crystals the values established for the crystallographic constants were:

$$\alpha = 63^\circ\ 19'\ 57'', \quad \beta = 128^\circ\ 52'\ 50'', \quad \gamma = 103^\circ\ 8'\ 48''.$$

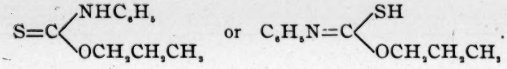
$$a : b : c = 0.6065 : 1 : 0.5513.$$

The principal angles for the identification of the substance would thus be:

$$001 : 100 = 57^\circ\ 24'\ 8''$$
$$001 : 010 = 108^\circ\ 37'\ 41''$$
$$010 : 100 = 99^\circ\ 59'\ 23''$$

In addition to the three pinacoids whose angles have just been given, the faces $\infty\bar{P}(1\bar{1}0)$; $2_1P(2\bar{2}\bar{1})$; $_1P_1\bar{\infty}\,(10\bar{1})$; and $\frac{4}{3}{}'P_1\bar{\infty}\,(04\bar{3})$ were observed. Of these the first two never showed a parallel (with the exception of a poorly developed one in a single instance); hence the presumption that the crystals are hemihedral.

The Compound of Phenyl Mustard Oil with Propyl Alcohol (Propyl Phenylsulphocarbamate),



Attempts were made to prepare this compound by heating molecular quantities of the mustard oil and propyl alcohol, in sealed tubes, at temperatures varying from 110° to 250° C., for periods of from three to six hours, but without success. In every case gaseous products were formed together with a quantity of thiocarbanilide ($S=C<^{NHC_6H_5}_{NHC_6H_5}$). After varying the conditions in many ways we finally found that the compound could be readily formed by heating the mustard oil and alcohol, in a flask provided with a return condenser, to the temperature of a boiling water-bath for several hours. Five grams of phenyl mustard oil and 5 grams of the pure normal propyl alcohol were thus heated for sixteen hours. The straw-colored liquid still had the odor of propyl alcohol, but on allowing it to stand in the cold it deposited long, white needles. These were filtered off, dissolved in benzene (in order to remove thiocarbanilide, which is practically insoluble in cold benzene), the benzene evaporated off, and the product recrystallized from absolute alcohol. The substance crystallizes in white needles belonging to the triclinic system, which melt at 48° C. It is easily soluble in alcohol, ether, chloroform, acetone, benzene, and acetic ether. Analyses gave the following results:

Determination of Nitrogen (Kjeldahl Method).

I. 0.4836 gram substance gave 0.04163 gram NH_3, corresponding to 0.03429 gram N.

II. 0.6087 gram substance gave 0.05217 gram NH_3, corresponding to 0.04297 gram N.

Determination of Sulphur (Carius Method).

I. 0.1956 gram substance gave 0.2341 gram $BaSO_4$.

II. 0.2126 gram substance gave 0.2559 gram $BaSO_4$.

	Calculated for $S=C<^{NHC_6H_5}_{OCH_3CH_2CH_3}$.	Found. I.	II.
N	7.191	7.059	7.09
S	16.421	16.44	16.53

These results show that the compound is the propyl ester of phenylsulphocarbamic acid.

Mr. Gignoux reports as follows concerning the crystallography of this substance :

Crystal system, triclinic.

The bright, colorless crystals are of acicular habit. The needles are six-sided, being bounded by three pairs of faces, whose angles are 68° 29′, 72° 06′, and 39° 25′. No end faces could be observed even though crystals were made from a number of solvents, including acetone, benzene, ethyl alcohol, amyl alcohol, and acetic ether. Since the extinction angle is oblique, however, the crystals can be definitely said to be triclinic even in the absence of terminal planes.

The Compound of Phenyl Mustard Oil with Isopropyl Alcohol (Isopropyl Phenylsulphocarbamate),

$$S=C<^{NHC_6H_5}_{OCH(CH_3)_2} \quad \text{or} \quad C_6H_5N=C<^{SH}_{OCH(CH_3)_2}.$$

Attempts were first made to prepare this compound by heating the components together in sealed tubes at varying temperatures, but without success. In every case thiocarbanilide, $S=C(NHC_6H_5)_2$, was the only solid product obtained. At the same time gaseous products were formed in considerable amount. This formation of diphenyl thiourea is probably due to the reaction between the phenyl mustard oil and the water formed from the alcohol. The alcohol, by loss of water, forms the ether (dipropyl ether) or the unsaturated hydrocarbon (propylene), and the phenyl mustard oil reacts with the water as follows :

$$2C_6H_5—N=C=S + 2H_2O = S=C<^{NHC_6H_5}_{NHC_6H_5} + H_2S + CO_2.$$

Using the same method which we employed in the case of propyl alcohol, and heating for twenty hours, we succeeded in

preparing the compound without trouble. The light-yellow liquid obtained deposited, in the cold, white crystals which, when freed from thiocarbanilide by dissolving in benzene and recrystallizing from alcohol, melted at 85°.5 C. It crystallizes in the monoclinic system and is soluble in alcohol, ether, chloroform, benzene, carbon bisulphide, and acetic ether. The following results were obtained on analysis :

Determination of the Amount of Nitrogen (Kjeldahl Method).

I. 0.3716 gram substance gave 0.03216 gram NH_3, corresponding to 0.02649 gram N.

II. 0.3788 gram substance gave 0.03284 gram NH_3, corresponding to 0.02705 gram N.

Determination of the Amount of Sulphur (Carius Method).

0.2082 gram substance gave 0.2493 gram $BaSO_4$.

	Calculated for $S=C<^{NHC_6H_5}_{OCH(CH_3)_2}$	Found. I.	II.
N	7.191	7.129	7.14
S	16.421	16.44	...

These results show that the substance is isopropyl phenylsulphocarbamate and that phenyl mustard oil reacts with secondary propyl alcohol as readily as it does with the primary alcohols of the paraffin series.

Mr. Ginoux reports as follows concerning the crystals of this compound :

Crystal system, monoclinic.

The habit of the brilliant, colorless crystals is very varied, in general conforming to one of three types : *a*, pyramidal, with a small base ; *b*, columnar, with their elongation parallel to the à axis ; and *c*, six-sided tabular, with the base as the principal face. From the measurements on 21 crystals the crystallographic constants were determined to be :

$$\beta = 87° 28' 50''. \quad \grave{a} : \bar{b} : \grave{c} = 0.6777 : 1 : 1.8325.$$

The faces commonly present are $+P,(\bar{1}11)$; $-P,(111)$; $oP,(001)$; $P\grave{\infty},(011)$; $\infty P,(110)$; and $\infty P\grave{\infty},(010)$.

The following are the angles :

001 : 110 = 87° 54′ 52″
001 : $\bar{1}$11 = 74° 53′ 24″
001 : 111 = 71° 04′ 31″
001 : 011 = 61° 21′ 19″
$\bar{1}$11 : 111 = 104° 42′ 21″
$\bar{1}$11 : $\bar{1}\bar{1}\bar{1}$ = 65° 34′ 54″
111 : 1$\bar{1}$1 = 64° 06′ 12″
111 : 110 = 16° 17′ 16″
$\bar{1}$11 : $\bar{1}$10 = 17° 11′ 44″
111 : 011 = 51° 35′ 45″
$\bar{1}$11 : 011 = 53° 06′ 36″
010 : 011 = 28° 38′ 41″

The monoclinic character of the crystals was confirmed by their optical behavior.

The Compound of Phenyl Mustard Oil with Isobutyl Alcohol (Isobutyl Phenylsulphocarbamate),

$S=C\begin{matrix}NHC_6H_5\\OCH_2CH(CH_3)_2\end{matrix}$ or $C_6H_5N=C\begin{matrix}SH\\OCH_2CH(CH_3)_2\end{matrix}$.

The isobutyl alcohol used was a pure product which boiled at 107° C. Heating the alcohol and mustard oil in sealed tubes at temperatures varying from 110° to 180° C., gave no solid product except thiocarbanilide. We therefore tried the method used with propyl alcohol, heating the two substances together for twenty hours. On cooling the yellow liquid a white crystalline substance was deposited, which was freed from thiocarbanilide by means of benzene, and recrystallized from absolute alcohol. It is soluble in alcohol, ether, benzene, carbon bisulphide, and chloroform, insoluble in water, and melts sharply at 80°.5 C. Analyses gave the following results :

Determination of the Amount of Nitrogen (Kjeldahl Method).

I. 0.3469 gram substance gave 0.028402 gram NH_3, corresponding to 0.02339 gram N.

II. 0.2873 gram substance gave 0.02375 gram NH_3, corresponding to 0.01956 gram N.

Determination of the Amount of Sulphur (Carius Method).

I. 0.1642 gram substance gave 0.1845 gram $BaSO_4$.

II. 0.1609 gram substance gave 0.1799 gram $BaSO_4$.

	Calculated for $S=C<^{NHC_6H_5}_{OCH_2CH(CH_3)_2}$.	Found. I.	II.
N	6.709	6.74	6.809
S	15.321	15.43	15.35

The product is therefore isobutyl phenylsulphocarbamate.

The Compound of Phenyl Mustard Oil with Tertiary Butyl Alcohol (Tertiary Butyl Phenylsulphocarbamate),

$S=C<^{NHC_6H_5}_{OC(CH_3)_3}$ or $C_6H_5N=C<^{SH}_{OC(CH_3)_3}$.

The tertiary butyl alcohol used boiled constantly at 83° C. The method of heating the two substances together in sealed tubes gave in every case thiocarbanilide and no other solid product. Heating the two products together on the water-bath, in a flask provided with a return condenser, for twenty hours gave a yellowish liquid from which long white needles separated out when placed in a freezing-mixture. These crystals dissolved again when the mixture was brought into a room at ordinary temperature, and could not then be again obtained. More of the material was then made, placed in a freezing-mixture as before, and as soon as the crystals separated out they were dried as quickly as possible on filter-paper and transferred at once to a weighed tube, which, after reweighing, was at once placed in the digestion flask. The following are the results of two analyses of this substance.

Determination of the Amount of Nitrogen (Kjeldahl Method).

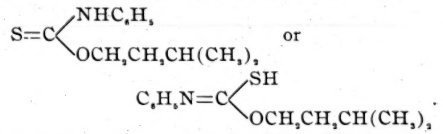
I. 0.8028 gram substance gave 0.060947 gram NH_3, corresponding to 0.050192 gram N.

II. 0.6221 gram substance gave 0.04808 gram NH_3, corresponding to 0.03959 gram N.

	Calculated for $S=C<^{NHC_6H_5}_{OC(CH_3)_3}$.	Found. I.	II.
N	6.709	6.25	6.36

These results show that the compound is tertiary butyl phenylsulphocarbamate and that tertiary alcohols react with the phenyl mustard oil just as readily as the primary and secondary compounds do.

The Compound of Phenyl Mustard Oil with Isoamyl Alcohol (Isoamyl Phenylsulphocarbamate),



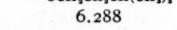
or

The isoamyl alcohol used was carefully purified and boiled constantly at 131° C. The phenyl mustard oil and the isoamyl alcohol were heated to boiling for some hours. The yellow liquid deposited white crystals on standing in the cold. As these crystals melt at ordinary temperatures they were removed from the liquid and pressed between filter-paper in the cold. When dried as completely as possible they were washed with a little alcohol and again dried between filter-paper. The product was soluble in alcohol and ether and melted at approximately 21° C. Analyses gave the following results:

Determination of the Amount af Nitrogen (Kjeldahl Method).

I. 0.3550 gram substance gave 0.029106 gram NH_3, corresponding to 0.02397 gram N.

II. 0.3360 gram substance gave 0.02539 gram NH_3, corresponding to 0.02091 gram N.

	Calculated for 	Found. I.	II.
N	6.288	6.75	6.22

The substance is therefore isoamyl phenylsulphocarbamate.

We next heated phenyl mustard oil with allyl alcohol in order to see if unsaturated alcohols react in the same way as the monacid alcohols of the paraffin series. The yellowish liquid deposited, on standing in the cold, a white crystalline substance melting at 236° C., insoluble in water but soluble in

alcohol and ether. This substance contained no sulphur, for when oxidized with nitric acid, according to the Carius method, it gave only a trace of barium sulphate. A determination of nitrogen by the Kjeldahl method gave the following result:

0.3113 gram substance gave 0.04755 gram NH_3, corresponding to 0.03916 gram N.

	Calculated for $OC<^{NHC_6H_5}_{NHC_6H_5}$	Found.
N	13.2	12.57

From these results it will be seen that the substance is symmetrical diphenyl urea. This was further proved by a determination of the boiling-point of the substance, which was found to be 262° C. The melting-point of diphenyl urea is 235° and its boiling-point 260° C.

Allyl alcohol, therefore, does not react with phenyl mustard oil to form a thiourethane.

The reaction of phenyl mustard oil with glycol and glycerin was next tried in order to see if the phenyl mustard oil could be used as a reagent for detecting the alcoholic hydroxyl group in polyacid alcohols. In both cases the only solid product formed was thiocarbanilide, as was shown by the analyses of the substance and a determination of its physical properties, and comparison of these with those of diphenyl thiourea, $SC(NHC_6H_5)_2$. This result is in accord with that of Tessmer and Volkmann,[1] who state that phenyl mustard oil reacts with glycerin to give diphenyl thiourea, due to the water which splits off from the glycerin. It is also in accord with the work of Snape, who states that phenyl mustard oil does not react with glycol to form a thiourethane.

With neither erythrite nor glucose nor with glycol chlorhydrin does phenyl mustard oil react, so that this substance cannot be used to detect the alcoholic hydroxyl group in polyacid alcohols.

We next took up the reaction between phenyl mustard oil and the phenols. As stated in the introduction to this article, both Dixon and Snape claim to have prepared a compound of phenyl mustard oil with phenol, though Snape found

[1] Ber. d. chem. Ges., 18, 972.

it impossible to prepare compounds with resorcin or hydroquinone. We first endeavored to repeat the work of Dixon and Snape and to effect the union of the mustard oil and phenol by heating the two substances together in sealed tubes. In every case, however, the tubes broke owing to the great internal pressure. By heating the two substances together to boiling for thirty-two hours and allowing the dark-red, syrupy liquid to stand in the cold, yellow needles crystallized out which melted at 152° C. These, when recrystallized from alcohol, were nearly white. They are nearly insoluble in ether and petroleum ether, readily soluble in alcohol, chloroform, acetone, and acetic ether, but difficultly in benzene. An analysis of the product purified by recrystallization from alcohol gave the following results:

Determination of Nitrogen by the Kjeldahl Method.

0.1390 gram substance gave 0.02095 gram NH_3, corresponding to 0.01726 gram N.

	Calculated for $S=C<^{NHC_6H_5}_{NHC_6H_5}$	Calculated for $S=C<^{NHC_6H_5}_{OC_6H_5}$	Found.
N	12.301	6.125	12.41
S	14.04	13.97	....

This compound is therefore thiocarbanilide and not the phenyl ester of sulphocarbamic acid. From the description of the compound given by both Dixon and Snape it seems highly probable that they obtained this same compound. They describe the compound they obtained as crystallizing in yellow leaves or needles, insoluble in ether and light petroleum, which agrees with thiocarbanilide and with our compound. Dixon gives the melting-point of his compound as 149°–151° C., while Snape found his to melt at 148° C. The melting-point of our compound was 152°, while thiocarbanilide melts at 150°.5 according to Lellmann, and at 153° according to Bamberger.

Unfortunately, both Dixon and Snape only determined the amount of sulphur in their compounds. Dixon found 13.48 per cent of sulphur, while Snape obtained 14.03 per cent, results which agree with that required for either thiocarbanilide

(14.04), or the phenyl ester of phenyl sulphocarbamic acid (13.97).

From the properties of the substance we obtained, as well as from the results on analysis, there can be no doubt that the substance is thiocarbanilide, and it seems highly probable that both Dixon and Snape obtained the same compound.

We then tried to bring about the union of phenyl mustard oil with hydroquinone and pyrogallol, but without success. Phenyl mustard oil does not, therefore, combine with phenols to form thiourethanes.

The aromatic alcohols also do not combine with phenyl mustard oil to form thiourethanes, for even when heated together for thirty-nine hours benzyl alcohol and phenyl mustard oil underwent no change; at least, no solid product could be isolated from the liquid.

It seemed desirable, in connection with this investigation of the action of phenyl mustard oil on alcohols and phenols, to determine whether this substance would combine with the acids of the paraffin and benzene series to form thiourethanes. We therefore heated 5 grams of phenyl mustard oil and 3 grams of acetic acid together on a water-bath, at 100°, for twenty-four hours. The only solid product obtained was a white crystalline substance melting at 236° and boiling at 262°. This compound was insoluble in water, only slightly soluble in chloroform, ether, and benzene, but soluble in acetone and alcohol. It is probably, therefore diphenyl urea.

With benzoic acid phenyl mustard oil does not combine when heated together on the water-bath for twenty-five hours. The benzoic acid dissolves in the hot phenyl mustard oil but crystallizes out again on cooling. With ethylidene lactic acid, phenyl mustard oil gave no thiourethane. The only products isolated after heating the two substances together for forty hours were thiocarbanilide (m. p. 154° C.) and carbanilide (m. p. 236°, b. p. 262°).

Acids therefore do not combine with phenyl mustard oil to form thiourethanes.

JUNE, 1899.

ON THE EFFECT OF VARIOUS SOLVENTS ON THE ALLOTROPIC CHANGE OF MERCURIC IODIDE.

By J. H. Kastle and Mary E. Clark.

Several years ago, in endeavoring to find some method other than that of sublimation, for the preparation of the yellow modification of mercuric iodide, it was observed by one of us (Kastle) that it could be prepared by dissolving the ordinary red modification in boiling amyl alcohol and allowing the solution to cool. Somewhat later Mr. Kemper studied the solution of sulphur and mercuric iodide in several high-boiling hydrocarbon solvents, such as naphthalene and pseudo-cumene. He observed that the red mercuric iodide dissolved quite freely in these solvents, especially above the transition-temperature of the iodide, to form yellow solutions, from which the yellow modification invariably crystallized out on cooling. It therefore occurred to one of us that it would probably prove interesting to study the action of a number of solvents, high- and low-boiling, on this compound. Altogether the action of 24 solvents has been studied. These, together with their boiling-points, are as follows:

Name of substance.	Boiling-point.
Ethyl bromide	38.8
Propyl chloride	48.0
Acetone	56.0
Ethylidene chloride	60.0
Ethyl iodide	72.0
Ethyl acetate	76.0
Ethyl alcohol	78.3
Isopropyl bromide	60.0
Benzene	80.0
Allyl alcohol	96.0
Toluene	110.0
Ethyl cyanide	115.0
Ethyl butyrate	121.0
Ethyl isobutyrate	110.0
Ethyl propionate	99.0
Amyl alcohol	132.0
Benzoic acid	249.0
Phenol	181.5

Name of substance.	Boiling-point.
Benzene cyanide	208.0
Oil of wintergreen	117.0
Propyl bromide	71.0
Pseudo-cumene	169.8
Naphthalene	218.0
Salol	....

In what follows, unless expressly stated to the contrary, the solubility of mercuric iodide is given for the hot solvent. In most cases it refers to its solubility at the boiling-point of the solvent.

Ethyl Alcohol.—Mercuric iodide is moderately soluble in absolute alcohol at its boiling-point. The solution had a decided yellow color, and on being placed in a freezing-mixture (ice and salt), yellow crystals separated from the solvent. These soon changed to the red modification. In order to determine whether the yellow variety alone crystallized from the solution, a drop of the solution was placed on the watch-glass and examined under a microscope. As a result of a number of such observations it was found that the yellow variety only separated from the solution, subsequently changing more or less rapidly to the red.

Amyl Alcohol.—Mercuric iodide dissolves very freely in hot amyl alcohol. A moderately concentrated solution prepared near its boiling-point was allowed to cool gradually. At 100° C. a large crop of lemon-yellow crystals separated from the solution. As the solution cooled further crops of yellow crystals were obtained. At 67° C. the first change of color was noticeable. Under amyl alcohol the yellow mercuric iodide is moderately stable. In two hours the solution had cooled down to 40° C. and about half the yellow had changed. After sixteen hours at ordinary temperature nearly all of the yellow had altered.

Allyl Alcohol.—Allyl alcohol dissolves mercuric iodide very freely, much more so than ethyl alcohol. The solution is yellow. On sudden cooling a large crop of lemon-yellow crystals is obtained. These were mostly of the needle-shaped variety, with some perfect rhombs. The yellow variety slowly changed to red. On allowing the solution to cool gradually a large number of rhombic crystals were obtained.

Acetone.—Mercuric iodide was found to be only slightly soluble in this solvent, much less so than in ethyl alcohol. The solution was yellow in color. On cooling irridescent yellow plates separated from the solution and rapidly turned red.

Phenol.—At 150° C. phenol dissolved mercuric iodide tolerably freely. A partially saturated solution at this temperature was found to have a yellow color and to deposit crystals on gradually cooling to 40°–50° C. The iodide crystallized out in yellow rhombs, together with numerous elongated and small fragmentary crystals.

Benzene.—Mercuric iodide is readily soluble in boiling benzene. A saturated solution of the iodide in this solvent is yellow in color. On being placed in ice-water, the solution gave considerable quantities of yellow crystals. These yellow crystals changed to red with great rapidity under this solvent, as all of them were completely altered in from two to three minutes.

Toluene.—Mercuric iodide is more soluble in toluene than in ethyl alcohol—color of the solution deep yellow. On cooling the hot solution a yellow precipitate was thrown down. In the first portions of this no crystalline structure was visible, even under the microscope. The last portions of the compound which were obtained from the solution were crystalline. The yellow precipitate rapidly changed to red.

Naphthalene.—Mercuric iodide is readily soluble in naphthalene at temperatures above its transition-point. A solution saturated at 160° C. and cooled to 150° C. gave yellow crystals. The solution in napthalene is yellow.

Pseudo-cumene.—Mercuric iodide is readily soluble in hot pseudo-cumene, giving a yellow solution. A solution in pseudo-cumene saturated at 143° C. gives, on slow cooling, very large and perfect yellow crystals.

Ethyl Iodide.—Mercuric iodide was found to be readily soluble in this solvent. Taken altogether, it is probably the best solvent for this compound of any yet tried. The solution was intensely yellow. On placing it in a freezing-mixture it yielded a large crop of yellow irridescent plates, which closely resembled lead iodide in appearance. On microscopic exam-

ination these crystals were found to consist of a very large number of rhombs, together with a number of elongated rhombic plates. Under the solvent the yellow variety quickly changed to red. On the other hand, some of the yellow crystals which had been obtained from this solvent and dried in the air at ordinary temperature, only slowly changed to red. In one batch of crystals a number of the yellow were found after two and one-half days.

Ethyl Bromide.—Mercuric iodide is only slightly soluble in this solvent, much less so indeed than in ethyl alcohol. It dissolves to form a pale-yellow solution, which, when cooled down in a freezing-mixture, gave a small crop of yellow, irridescent, rhombic plates. Those that had been formed by sudden cooling were found to be very stable under the solvent, the change to red being complete only after standing twenty-four hours. The crystals obtained by allowing the solution to cool down gradually were found to alter more easily than those obtained by sudden cooling.

Isopropyl Bromide.—Mercuric iodide is only sparingly soluble in isopropyl bromide, giving a solution which in small amounts appears colorless. This is probably due to the small amount of the yellow compound in solution. From this solution, on sudden cooling, mercuric iodide separates out in yellow rhombs, also in numerous small fragmentary crystals. The whole mass slowly changed to red.

Isobutyl Bromide.—Mercuric iodide is only moderately soluble in this solvent. It gives a pink solution, from which, on sudden cooling, it gives a crystalline yellow precipitate, which is composed of very minute, fragmentary crystals. On gradual cooling the compound crystallizes out in the form of yellow needles, which slowly change to red.

Ethylidene Chloride.—Mercuric iodide is only slightly soluble in this solvent. The solution in small amounts is colorless. On sudden cooling at 18° C. the iodide crystallizes out in yellow plates, which quickly change to red.

Propyl Chloride.—This solvent dissolves mercuric iodide very sparingly, giving a pink solution. On cooling yellow crystals were obtained, which, under the microscope, were seen to consist of rhombs and rhombic plates.

Ethyl Cyanide.—Mercuric iodide dissolves very readily in ethyl cyanide, even more so than in ethyl alcohol. This solution is yellow, and on sudden cooling deposits yellow crystals, which were found to consist of rhombs and rhombic plates, and which were found to change to red with considerable rapidity. On gradual cooling the same form is obtained, only the crystals are larger.

Benzene Cyanide.—Mercuric iodide is only moderately soluble in benzene cyanide, but very little more so than in ethyl alcohol. It gives a deep-yellow solution, which, on sudden cooling, deposits yellow crystals, rhombs, rhombic plates and needles, which rapidly turn red. A solution on gradual cooling deposits yellow crystals, in which there are no needles, and in which the number of rhombs is greater; the solution in each case was obtained above the transition temperature of mercuric iodide.

Benzoic Acid.—Mercuric iodide dissolves in benzoic acid very rapidly at high temperatures. In fact, it proved one of the best solvents tried on this substance. A saturated solution was prepared at 180° C. The solution was yellow, and on gradual cooling, at 152° C., gave a large crop of crystals in the form of yellow irridescent plates.

Ethyl Acetate.—This solvent dissolves mercuric iodide very sparingly, much less readily than alcohol. It gives a yellow solution, from which crystals are deposited in the form of yellow irridescent plates.

Ethyl Propionate.—This solvent dissolves mercuric iodide fairly easily, and somewhat better than ethyl alcohol and ethyl acetate. The solution was found to have a light yellow color and to deposit crystals, even when warm, in the form of yellow needles.

Ethyl Butyrate.—Mercuric iodide was found to be very soluble in this solvent. The solution, made by saturating with the iodide at 150° C., was found to be yellow in color. On sudden cooling the iodide crystallized from this solution in large numbers of thin, prismatic crystals, yellow in color, and wanting in irridescence. On gradual cooling needle-shaped crystals of the yellow iodide were again obtained. Under the solvent these crystals were found to change to red very slowly,

whereas the same crystals when exposed to air, out of contact with its solvent, altered very rapidly.

Ethyl Isobutyrate.—Mercuric iodide is soluble only to a moderate degree in this solvent, much less soluble than in ethyl butyrate, but soluble to about the same amount as in ethyl alcohol. It forms a pale-yellow solution in this solvent, and on sudden cooling crystallizes out in quantities of yellow needle-shaped crystals. On cooling gradually large numbers of perfect yellow rhombs are formed, especially at 100° C. These rhombs were found to alter in color more rapidly than the needle-shaped crystals. The yellow crystals changed more rapidly than those obtained from the butyrate, but less rapidly than those from ethyl propionate.

Methyl Salicylate (*Oil of Wintergreen*).—Mercuric iodide dissolves very readily in this solvent. At 117° C. a solution was prepared having a deep-yellow color. On sudden cooling yellow crystals are formed, which were found to consist mainly of the needle-shaped variety. These were found to be very stable. Some of the needle-shaped crystals were placed on a watch-glass and allowed to remain undisturbed for some time. The greater number of these were found to be unaltered after thirty-two hours, and some of them were unchanged after three days. On allowing the solution to cool gradually, yellow needles crystallize out while the solution is still warm, which are larger and finer than those obtained on sudden cooling; also about an equal number of rhombs and rhombic plates are obtained. The first portions that crystallize out consist almost entirely of needles, while the last portions consist almost entirely of rhombs and rhombic plates.

Phenyl Salicylate (*Salol*).—This substance dissolves mercuric iodide very sparingly at 145° C. The solution is yellow, and on sudden cooling the iodide crystallizes out in the form of small, yellow, needle-shaped crystals, which gradually change to red. On cooling slowly the iodide is obtained in the form of very long, thin, needle-shaped, yellow crystals, which very slowly change to red.

It will be seen from the above that solutions of mercuric iodide, with the exception of two, produced with alkyl

halides, have a yellow color,[1] and that all solutions, without exception, deposit yellow crystals on cooling. Bancroft[2] has observed that water precipitates the yellow modification from a solution of mercuric iodide in methyl alcohol, and from this he drew the conclusion that on sudden precipitation the unstable form is the first to appear. It is also well known that mercuric iodide is yellow when first produced by double decomposition from aqueous solutions. It has been noted in the above that several solutions of mercuric iodide which deposit yellow crystals are themselves pink in color. Such solutions have been obtained with bromoform, ethylene bromide, propyl chloride, and isobutyl bromide. At first these were thought to be solutions of the red modification. On more careful examination, however, it was found that the pink color was not due to the red modification of the mercuric iodide, but to the formation of unstable alkyl iodides, which exhibit a pink coloration in the first stages of their decomposition. These unstable alkyl iodides are produced in such solutions by partial double decomposition with the mercuric iodide,

$$2C_3H_7Cl + HgI_2 = 2C_3H_7I + HgCl_2.$$

It will be observed that these pink solutions were only obtained with the alkyl halides as solvents. It would seem that the color of the red iodide of mercury is such that it ought to give red or pink solutions. The fact that only yellow solutions were obtained by dissolving the red iodide in these various solvents, and that the yellow modification alone crystallizes out of these solutions, would seem to indicate that in the act of solution, the transition-point of mercuric iodide (128° C.) is greatly lowered, for the production of these yellow solutions occurs with low- as well as with high-boiling solvents, the lowest boiling solvents tried being ethyl bromide 38°.4 C., propyl chloride 48° C., and acetone 56° C. In order to form a better idea of the change which occurs when the red mercuric iodide passes into solution, the following

[1] In an article on "The Color Relations of Atoms, Ions, and Molecules," M. Cary Lea, Chem. News, **73**, 260, describes a solution of mercuric iodide in alcohol as absolutely colorless. He evidently failed to compare the color of this solution with that of the pure solvent.

[2] Jour. Phys. Chem., **1**, 142 (1896).

experiments were tried with amyl alcohol: A quantity of pure crystalline red iodide of mercury was put in a tube with amyl alcohol, the former being in excess of the amount required to form a saturated solution at the temperature of the experiment. The tube was then sealed and heated in a current of steam. Tubes of this character were heated for one, two, three, and eight hours. A yellow solution of mercuric iodide was obtained in each case, and invariably a thin film of the yellow variety, or a little mass of yellow crystals was found on top of the unchanged red iodide. Further, when such tubes were cooled, either gradually in the air or by plunging into cold water, crystallization always started on the top of the undissolved mass; that is, the small amount of the yellow variety already in the tube served as a nucleus for crystallization. After a time the solution above the unchanged red variety became filled with yellow crystals, and, on standing, these also changed to red, the change taking place in every instance from the surface of contact with the red up, indicating that the yellow changes quickest in contact with the red modification. In such tubes the difference between the two varieties of the compound is so striking and the line of demarcation between the two so sharp as to make this a beautiful method for exhibiting these two varieties of the iodide. It would seem, therefore, that when amyl alcohol is brought together with the red modification in excess, a certain number of molecules of the red modification of the iodide change to yellow and at once pass into solution. When equilibrium is reached, however, there are as many molecules passing out of the solution as are passing in, and these are also of the yellow variety. That such is the case is seen from the small mass or film of yellow crystals, which is invariably formed by heating the solution of mercuric iodide in contact with an excess of the red variety of this compound. That the red variety is not entirely changed to yellow by first passing into the solution and then crystallizing out is probably due to the fact that, by contact with a certain amount of the red variety remaining in the tube, the yellow is rapidly changed to red as it separates from the solution. Hence we would have the solvent constantly changing the red modification to

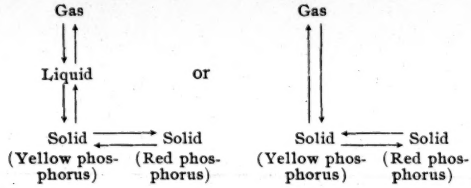
yellow and dissolving it and again precipitating it. This last, however, would tend to pass back to the red as soon as removed from the solution. The idea that red mercuric iodide itself is insoluble in these various solvents would seem to derive support from the insolubility of allotropic modifications of other substances. As is well known, red phosphorus is insoluble in most solvents, and from solutions in the few solvents in which it is soluble, only yellow phosphorus can be obtained. Then again, the remarkable insolubility of the several forms of carbon, the transition temperature of which is probably very high, is interesting and suggestive in view of these considerations. In dealing with the facts set forth in the above, it is almost impossible to avoid the much-discussed question: *What is in the solution?* In the case of sulphur two entirely different answers have been given to this question. As the result of his investigations Deville[1] came to the conclusion that there was a distinct difference in solutions of sulphur. This, however, has been denied by others, among them Ostwald. In the latter's "Outlines of General Chemistry," English Translation, p. 191, we find the following bearing on this point: "When allotropic solids are brought into the liquid or gaseous state not a trace of difference between them is left. The vapor of red phosphorus is identical with the vapor of yellow phosphorus, and a solution of rhombic sulphur in carbon disulphide is in no respect different from a solution of similar composition made from monosymmetric sulphur. Conversely, from the same solution, *e. g.*, one of nickel sulphate supersaturated by cooling, any one of the different forms of the salt may be obtained by the introduction of a fragment of the corresponding crystal. The so-called physical isomerism thus occurs exclusively in connection with the solid substance, and disappears whenever the latter assumes another state of aggregation."

Unfortunately in spite of their clearness, these considerations do not afford a sufficient explanation of the changes occurring in the solution of mercuric iodide. It is certain that one characteristic property of the yellow variety of mercuric iodide is still preserved when it goes into solution. This is its

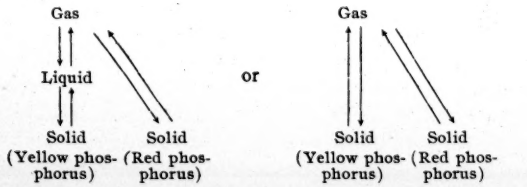
[1] Compt. rend., **26**, 117 (1848).

yellow color. While this solution can be made by starting with either the red or the yellow modification, the converse of this is not true. A crop of red crystals is not obtained by the introduction of a red crystal into the solution, but crystals of the yellow variety only. This has been shown in experiments with amyl alcohol.

The conclusion, therefore, seems logical that solutions of mercuric iodide really contain the yellow modification of this compound and not simply molecules of HgI_2, which may arrange themselves in the yellow or red modification of this compound according to the nature of the crystal form which is first presented to them. In the case of phosphorus, for example, it is quite probable that nothing is known of red phosphorus as a gas or in solution, for the reason that the conditions necessary to change it into the gaseous state or to cause it to pass into solution, probably first change it into the yellow variety.[1] These changes might be represented in this way:

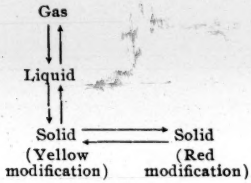


and not

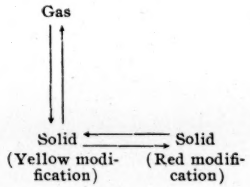


So, in the same way, on vaporization and solution and the reverse, the changes occurring in the red iodide of mercury might be represented thus:

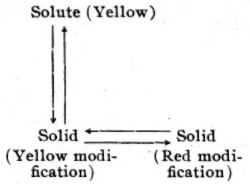
[1] Comey's Dictionary of Chemical Solubilities, p. 317 (1896).



Or in the event of sublimation, thus:



Or by solution, thus:



It is interesting to note, in this connection, that mercuric iodide, both as a gas and solute, is yellow in color. It would seem, therefore, that the yellow modification of mercuric iodide (solid) is identical with that which exists in its solutions, or is perhaps a polymer of the same.

Since this article went to press our attention has been called to some recent work by Gernez[1] on the vaporization of mercuric iodide in vacuo. He has shown that the vapor given off at all temperatures by the yellow variety of this compound deposits yellow orthorhombic crystals, no matter what may be the temperature of the cooler surface on which the deposition occurs. The yellow crystals are also obtained from the vapor

[1] Compt. rend. (1899), 128, 1516, 1519.

emitted by the red variety when vaporized at any temperature from 25° C. up to the transition temperature. If, however, the cool surface is slightly rubbed with the red crystals, the form deposited is also red. It is believed that these results of Gernez present nothing at variance with the views advanced in the above.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, KY., Sept., 1899.

Contribution from the Kent Chemical Laboratory of the Yale University.

THE ETHERS OF ISONITROSOGUIACOL IN THEIR RELATION TO THE SPACE ISOMERISM OF NITROGEN.

BY JOHN L. BRIDGE AND WM. CONGER MORGAN.

When the presence of isomerism in the quinoneoximes was first noted by one of us[1], and the phenomenon exhibited by the two isomeric ethers then described was shown by Kehrmann[2] to be due to no structural differences, but to necessitate the assumption of a spatial arrangement about the nitrogen atom, according to the theory of Hantzsch and Werner, the plan was adopted of studying the various substituted quinoneoximes, by means of their acyl and alkyl ethers, with reference to this phenomenon. Accordingly we have investigated the toluquinoneoximes[3], both ortho and meta, producing them by the action of nitrous acid on the cresol as well as by hydroxylamine on toluquinone, and found that, whereas there is abundant evidence for the existence of stereoisomeric bodies in the metaoxime ethers, in the derivatives of the orthooxime, all such indication is wanting. The significance of this observation is furthermore increased by the fact that all oximes, in which isomerism has been reported, may be considered as derivatives of metasubstituted quinones, and it seemed not improbable, therefore, that these observations might be formulated into a general rule regarding the appearence of isomerism in the quinoneoximes.

In the course of his investigation of the properties and re-

[1] Ann. Chem. (Liebig), **277**, 79. [2] *Ibid.*, **279**, 27.
[3] This JOURNAL, **20**, 761; **22**, 402.

actions of isonitrosoguiacol, among other derivatives, Pfob[1] made the methyl and acetyl ethers, but did not announce the observation of any cases of isomerism. Isonitrosoguiacol may be considered as the metamethoxyquinoneoxime, hence this metasubstituted quinoneoxime presented conditions differing widely from the other members of the same series above mentioned. Moreover, because of its close relationship to toluquinonemetaoxime, from which it differs only by the interposition of an oxygen atom between the ring and the methyl group, it seemed possible that isomeric modifications of the ethers might exist, which had been overlooked by the former investigator. When, furthermore, Rupe[2] made no mention of such appearence in his research on isonitrosoguiacol, it seemed advisable to undertake anew the investigation of this body with the special purpose of discovering such isomerism, if possible, and to couple with it an investigation of the orthomethoxyquinoneoxime or isonitroso derivative of the monomethyl ether of resorcin, in order by this means to be able to parallel in these closely analogous bodies the experiments with the ortho- and metacresols.

With this idea, the work of Pfob and Rupe was carefully repeated, so far as it pertained to the question in hand, but, aside from minor differences, our results served only to corroborate the testimony of these investigators. New derivatives, to be described later, were prepared in the hope that these bodies might show some variations leading to the discovery of isomeric modifications, but each appeared to be entirely homogeneous and no evidence for isomerism could be found. These results are of course only negative and do not disprove the existence of space isomers in the same bodies, yet the same methods, which gave very positive evidence of their presence in other quinoneoxime ethers, were used to detect them in this instance.

Aside from the difficulty of obtaining pure monomethyl ether of resorcin in any considerable quantity, because of poor synthetical processes and inefficient methods of separation, inasmuch as preliminary experiments pointed to a multiplicity of

[1] Monatsh. Chem., 18, 467. [2] Ber. d. chem. Ges., 30, 2444.

products in the reaction with nitrous acid such as Kietaibl[1] found with the monoethyl ether, it was thought inadvisable in the light of the results obtained with the meta body, to continue the work on the ethers of orthomethoxyquinoneoxime. Work along the general line will be continued, and the results of experimentation with mononitrosoresorcin will soon appear.

EXPERIMENTAL PART.

Isonitrosoguiacol and Salts.

The isonitrosoguiacol used in the investigation was prepared both by the method of Pfob, working with nascent nitrous acid in alcoholic solution, and also by the general method for the formation of the sodium salts of isonitroso bodies suggested by Walker.[2] To a concentrated alcoholic solution of sodium alcoholate, guiacol is added in sufficient quantity to form the sodium salt by the resulting metathesis, then, to this solution of sodium guiacol, slightly more than the theoretical quantity of amyl nitrite is added and, after thorough mixing, the liquid is allowed to stand over sulphuric acid for twenty-four hours, when the bright olive-green crystalline sodium salt of isonitrosoguiacol separates. After washing thoroughly with ether, pulverizing and rewashing, the salt may be used directly for the preparation of derivatives, or, if further purification is desirable, it may be dissolved in water, acidified with hydrochloric acid, and the filtered and dried product dissolved in ether and shaken with animal charcoal, when, upon evaporation, the pure isonitrosoguiacol crystallizes. Of the above methods of preparation the latter is much to be preferred, although Rupe mentions it unfavorably because of poor yields and impure products. He advocates the use of ethyl nitrite in a closed tube ; but on trial we were unable to obtain the quantitative yields which he reports and the seventy per cent yield which the amyl nitrite gives, makes this method quite equal, in efficiency as well as purity of reaction-product, to the other more tedious process.

The silver salt, formed from the sodium salt by treating the aqueous solution with a slight excess of silver nitrate, comes

[1] Monatsh. Chem., 19, 536. [2] Ber. d. chem. Ges., 17, 399.

down as a brown gelatinous precipitate, which becomes crystalline on gently warming, or may be obtained in crystalline form at once by heating the separate solutions to 50° C. before mixing. It is a very unstable salt, the dry product decomposing with a very gentle heating.

Isonitrosoguiacol Benzoyl Ether.

The sodium salt formed as above was dissolved in as little water as possible and four or five times its volume of alcohol added. This solution was thoroughly shaken with a slight excess of benzoyl chloride, added drop by drop. The reaction is immediate and the ether soon begins to come out of the solution in almost pure condition. Recrystallized from alcohol, it separates in straw-colored, branching crystals, which melt sharply at 188° C. when "dipped" for ten seconds. Heated gradually from normal temperatures, it begins to decompose at 175° C. and liquefies at 185°–188° C., the temperature depending on the rapidity with which heat is applied.

Fractional crystallization from alcohol or other solvents did not essentially change the melting-point, nor were any different phenomena observed when the isonitrosoguiacol was made by the acid reaction. This ether dissolved readily in chloroform and glacial acetic acid, much less in benzene and ligroin, and is practically insoluble in ether and carbon disulphide. On analysis:

0.1100 gram of the substance, dried over H_2SO_4, gave 0.2632 gram CO_2, and 0.0428 gram H_2O.

0.1205 gram of the substance gave 5.45 cc. N at 15° C. and 772 mm. pressure.

	Calculated for $C_{14}H_{11}O_4N$.	Found.
C	65.34	65.26
H	4.31	4.32
N	5.46	5.38

Isonitrosoguiacol Benzoyl Ether Dibromide.

Three grams of the benzoyl ether were dissolved in 25 cc. of chloroform and 2 grams of bromine were added, the mixture being kept cool by running water. The solution was

allowed to stand for from one to two hours and then to evaporate spontaneously. The dibromide is left behind as a light-brown substance. Attempts to crystallize from glacial acetic acid proved unsatisfactory, since the boiling solvent caused a decomposition of the ether; nor did a solution in fuming nitric acid, precipitated by water, give a pure white product. The best results were obtained by washing with warm dilute alcohol when the product becomes yellowish-white, and melts at 153°–154° C., browning considerably above 140° C. An analysis of the substance purified in this manner shows a low percentage of bromine.

0.1052 gram of the substance, dried over H_2SO_4, gave 0.1547 gram CO_2, and 0.0284 gram H_2O.

0.0509 gram of the substance gave 0.0449 gram AgBr.

	Calculated for $C_{14}H_{11}O_4NBr_2$.	Found.
C	40.29	40.10
H	2.66	3.00
Br	38.34	37.52

Monobromisonitrosoguiacol Benzoyl Ether.

By boiling the white dibromide with 60 per cent alcohol for three-quarters of an hour, the halogen acid and a bright-yellow monobromine compound are formed. This ether crystallizes from boiling alcohol in the characteristic prismatic form of such bodies and melts with decomposition at 178° C. Repeated recrystallizations did not change this melting-point and no indication was noted suggesting the possibility of a mixture. On analysis:

0.1317 gram of the substance, dried over H_2SO_4, gave 0.2410 gram CO_2, and 0.0368 gram H_2O.

0.2101 gram of the substance gave 0.1172 gram AgBr.

	Calculated for $C_{14}H_{10}O_4NBr$.	Found.
C	49.99	49.91
H	3.00	3.11
Br	23.79	23.75

TEXAS PETROLEUM.

By F. C. Thiele.

It has long been known that mineral oil existed in the State of Texas, but only of late has this discovery been utilized. About three years ago oil was discovered in the town of Corsicana, and further researches proved that Corsicana was literally built on a vast oil-pool. About 400 wells are in operation at present. A big refinery was built to dispose of the natural product, and Corsicana is a flourishing town to-day. All this was accomplished in the short space of a couple of years through an accidental discovery.

The Corsicana oil, as it comes from the wells, resembles in its appearance the Lima-Ohio oil, without having, however, the disagreeable odor, so characteristic of the oil found in the Ohio-Indiana district. An analysis made by the author shows the Corsicana oil to be composed as follows:

Crude Oil—Specific Gravity = 0.8296.

	Per cent.	Specific gravity.
Naphtha	10.8	0.710
Kerosene	54.5	0.796
Residue	34.7	0.905
	100.0	

A more elaborate analysis made by Mr. E. H. Ernshaw shows the following composition of the Corsicana oil.

Oil very dark-brown and opaque, but thin and fluid at 60° F. Specific gravity at 60° F. = 0.8292.

	Temp., °F	Percentage by volume.	Percentage by weight.	Specific gravity at 60° F.	Color, etc.
A	130–200	2.80	2.24	0.6653	Colorless
B	200–250	5.10	4.31	0.7017	
C	250–300	7.60	6.69	0.7302	
D	300–350	8.20	7.44	0.7527	
E	350–400	9.40	8.75	0.7718	
F	400–450	7.40	7.07	0.7920	
G	450–500	8.30	8.09	0.8088	
H	500–550	6.45	6.43	0.8260	Very faint yellow
I	550–600	7.75	7.85	0.8404	" " "

	Temp., °F.	Percentage by volume.	Percentage by weight.	Specific gravity at 60° F.	Color, etc.
J	600–650	14.95	15.43	0.8555	Yellow
K	650–665	17.25	18.07	0.8687	Deep reddish-yellow
L	over 650	1.30	1.41	0.8972	Deep red—solid
M	over 650	1.40	1.63	0.9699	Dark red-brown—solid
	Residue	....	2.63	.....	
	Total	97.90	98.04		

The above analysis shows the Corsicana oil to be closely related to Pennsylvania oil, especially that of the Washington district, but it contains, according to my researches, a certain amount of asphaltum or bodies very similar to it. The presence of asphaltum compounds in crude oils can easily be demonstrated by the addition of tin tetrachloride, $SnCl_4$, to a sample of the oil in question. If a black precipitate is formed on the addition of the reagent, asphaltum or similar compounds are present in the oil. I found this reaction to be of value for oils which are subjected to distillation, as oils containing asphaltum should be distilled with great care and a very gradual rise of temperature, so as not to get too large an amount of the terpene-like decomposition-products of the asphaltum in the distillates. The presence of these bodies, which resemble aromatic hydrocarbons, tend to color the oil yellow, and even a very effective acid treatment does not seem to improve the oil much in color. This behavior of the distillates resembles the one which oils show when they have been subjected to overheating, as in the case of certain desulphurizing processes, proposed for the purification of strongly sulphur-bearing oils, such as Lima, Canadian, and others.

It was soon found, after the Corsicana oil field was discovered, that oil existed in other places in Texas, and borings for it were rapidly made in a number of places. It soon developed that a well-defined oil stratum existed, which, following the Trinity river to Nacogdoches, and turning here and following the Sabine River, flowed out into the Gulf of Mexico at Sabine Pass, covering the water at times with a black greasy substance over quite a large area.

The oil found at Nacogdoches is very heavy, its specific gravity being 0.915. Its color is black, and it is strongly im-

pregnated with sulphuretted hydrogen. It occurs in shallow wells not over 90 feet deep, and very likely belongs to the class of oils which are described in the literature as maltha.

From Nacogdoches, going south, the oil makes its next appearance at Rockland, the terminus of the Rockland, Sabine Pass Railroad. It is asserted that the oil exists here in large quantities, but no researches regarding its properties have been made. Saratoga, south of Rockland, is the next place where oil deposits are found, and experimental boring has been going on here for some time. The oil found here is still heavier than the Nacogdoches oil, having a specific gravity of 0.955. It is a black oil rich in asphaltum.

Fourteen miles south of Saratoga is the watering-place of Sour Lake, where a large oil deposit occurs. The soil at Sour Lake is undoubtedly of volcanic character, judging by the large variety of waters found here, and the general condition of the territory.

The crude petroleum found at Sour Lake occurs at a depth of 250 feet in the alluvial formation, and is what is termed a "surface oil." Its specific gravity at 63°.5 F. is 0.963, which is the highest specific gravity observed with any crude oil found on the western hemisphere. A fractional distillation of the oil shows the following constituents:

Fraction.	Temperature, °F.	Percentage by volume.	Specific gravity.	Color, etc.
1	.....	....	....	
2	212–266	0.07	....	Yellow
3	266–320	0.03	....	"
4	320–392	1.59	0.684	"
5	392–572	19.49	0.840	" blue fluorescence
6	.....	....	....	
7	572–641	5.15	0.782	Dark-yellow
Residue		71.11	0.978	Black
Total		97.44		

The oil contained 20 per cent asphaltum.

The analysis was carried out according to the directions laid down by R. Kissling during his investigations of crude oils of different origin.

The above analysis indicates that the greater part of the oil is composed of hydrocarbons excellently suited for lubricating

purposes, and the last fraction has a viscosity of 19° (Engler apparatus), a figure which exceeds that of the heaviest Russian products. Tests which were made on the large scale showed the presence of aromatic hydrocarbons, such as pseudocumene and others, and according to its behavior the crude oil may be called a true representative on American soil, of the oil found at Wietze-Steinförde, Germany, which was pronounced by Prof. Engler one of the most valuable sources of high-grade lubricating oils, if it could be freed of its asphaltum by proper refining and treatment. Solid paraffin has not been found in the crude oil, nor in any of the refined products, and it is doubtful whether any is present.

As to the origin of the oil, the presence of aromatic hydrocarbons and the absence of solid paraffin would indicate a vegetable origin, but, on the other hand, nitrogen products and a large amount of sulphur have been found in the oil, and these facts favor the view that it is of animal origin.

I cite here a test which I made to further advance the knowledge of this interesting oil. Some of the oil was dissolved in benzene, C_6H_6, which dissolved it with the separation of some water. The latter was removed and alcohol of 85 per cent added until no further precipitation occurred. The whole was well shaken, and after standing for some time the supernatant clear liquid was removed from the black resinous mass formed on the bottom of the vessel. The clear liquid was evaporated on a water-bath at a temperature of 80° C. A very viscous oil remained behind, which, when heated to 120° C., gave a very decided odor of musk.

The black resinous mass, dried at 120° C. for several hours, presented, after cooling, the general properties of "goudron," but had an odor which could not be distinguished from rancid stearin. This distinguishing feature recalls some experiments which were published in the "Chemiker Zeitung" several years ago on the distillation of so-called "stearin-pitch." Products were obtained which resembled in every respect the distillates obtained from mineral oils. As stearin is undoubtedly of animal origin, the above discovery may furnish further evidence of the correctness of the theory of Höfer and Engler.

It has often been asserted that the water which comes up with the crude oil when the latter is pumped out of the well does not contain any sulphates or merely traces of them. C. Ochsenius especially expressed this opinion very strongly and tried to prove that such was the case in every instance. The conditions are, however, different in Sour Lake. As I have stated already the character of the territory there is undoubtedly volcanic, and numerous water wells occur there which are very strong in sulphates, especially alumina, and contain in many instances large amounts of free sulphuric acid. The water coming out of the ground carries with it considerable oil, which floats on it as a thick black tar. The oil wells which were sunk artificially contain water, which is strong in chloride of sodium, but still contains a considerable amount of sulphates. Whether the occurrence of this large amount of sulphates and free sulphuric acid is related to the genesis of the oil or not is an open question, but as the opinions are still divided on this subject I deemed it necessary to mention the facts as they are presented by nature.

NOTE.

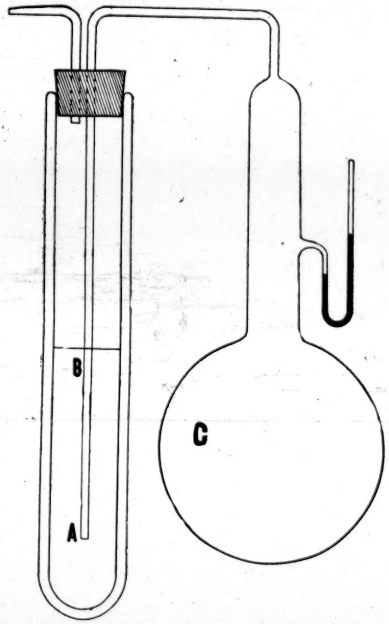
Solid Hydrogen.

In a recent number of the *Chemical News*,[1] Dewar describes the method by which he solidified hydrogen. He at first attempted to secure it by suspending a Dewar vacuum tube, partly filled with liquid hydrogen, inside of a larger vacuum tube containing the liquid hydrogen, and evaporating the liquid under diminished pressure. All the experiments carried out in this way failed, probably on account of supercooling of the liquid. By working under different conditions, however, he succeeded in obtaining the solid material and showed that it has no metallic character, but must be classed among the non-metallic elements.

The apparatus which he used was as follows: "A flask, *C*, of about a liter capacity, to which a long glass tube bent twice at right angles was sealed, as shown in the illustration, and to which a small mercury manometer can be sealed, was filled with pure dry hydrogen and sealed off. The lower portion, *AB*, of this tube was calibrated. It was surrounded with liquid hydrogen placed in a vacuum vessel arranged for

[1] Chem. News, 80, 132.

exhaustion. As soon as the pressure got well reduced below that of the atmosphere, perfectly clear liquid hydrogen began to collect in the tube AB, and could be observed accumulating until, at about 30 to 40 mm. pressure, the liquid hydrogen surrounding the outside of the tube suddenly passed into a solid, white, foam-like mass, almost filling the whole space. As it was not possible to see the condition of the hydrogen in the interior of the tube AB, where it was covered with a large



quantity of this solid, the whole apparatus was turned upside-down in order to see whether any liquid would run down AB into the flask C. Liquid did not flow down the tube, so the liquid hydrogen, with which the tube was partly filled, must have solidified. By placing a strong light on the side of the vacuum test-tube opposite the eye, and maintaining the exhaustion to about 25 mm., gradually the solid became less

opaque, and the material in AB was seen to be a transparent ice in the lower part, but the surface looked frothy." The melting-point of hydrogen must be about 16° or 17° absolute, and the limit of temperature which can be obtained by the evaporation of solid hydrogen is from 14° to 15° absolute.

J. E. G.

REVIEWS.

INORGANIC CHEMICAL PREPARATIONS. By FELIX LENGFELD, Assistant Professor of Inorganic Chemistry in the University of Chicago. New York: Macmillan Co. 1899. 55 pp.

This little manual indicates the spread of the newly-revived custom of making inorganic preparations an essential part of the laboratory work. There is nothing new in the idea. In the Göttingen laboratory and in other German laboratories during Wöhler's lifetime, inorganic preparations were made by every student, but since then, in nearly all laboratories, the number required has been gradually reduced to the few elementary gases and simple salts now generally required.

Hugo Erdmann's manual, published at Halle in 1893, was the first attempt to revive the custom. Confining ourselves to this country, Johns Hopkins adopted a privately printed manual in 1894; Vulté and Neustadt, of Columbia, published one in 1895; and F. H. Thorp, of the Massachusetts Institute of Technology, another in 1896. As to the present book, Professor Lengfeld has made an excellent selection; he expects the student in each case to study the original article to which he gives the reference. Thus his book is especially addressed to advanced students, though it would be available for others with an instructor's help. It can be cordially recommended.

E. R.

THE CHEMISTRY OF SOILS AND FERTILIZERS. By HARRY SNYDER, B.S., Professor of Agricultural Chemistry, University of Minnesota, and Chemist of the Minnesota Agricultural Experiment Station. Easton, Pa.: Chemical Publishing Co. 1899. 277 pages. Price, $1.50.

In the present age of competition, when every method of artificial production is being pushed to its limit, as far as the yield is concerned, the skill of the scientist has been called to aid this development. For various reasons the farmer has, of all classes, probably availed himself least of this aid and is still, in many cases, carrying on his work by methods which have been shown to be more injurious than beneficial. It is questionable whether the efforts of the Agricultural Experiment Station to overcome these difficulties and to aid the farmer have met with the desired results, on account of the unintelligible form in which the information is often supplied to him.

Within the last few years the farmers in many sections have realized that much material is being lost through their lack of knowledge of the principles of the changes taking place in the soil, and the scientific application of fertilizers. By the aid of farmers' conferences and short courses of instruction by trained experts on well-arranged experimental grounds, many farmers have learned to carry on their work in a scientific manner and to supply the waste by the right material in the right amount. The author of this book uses it as a guide in a course given to men who expect to become farmers. If all the young men who expect to follow this profession would take such a course of instruction, it would not be many years before the cultivation of the soil would be carried on in as scientific and business-like a manner as it is in many parts of Europe, where land is dear, and the most improved methods must be used to produce financial success. An idea of the general ground covered by this book can be seen from the headings of the chapters. The subject is treated under the following heads: The classification of soils, physical and chemical properties; nitrogen, its uses, methods of formation, occurrence and fixation; various classes of manures and fertilizers; and requirements and rotation of crops. The book is written in such a way as to be intelligible even to one who has had no scientific training, and it would be well for every farmer to read it, as it might stimulate him to study the problems more thoroughly, and put in practice many of the suggestions.

J. E. G.

PRACTICAL METHODS FOR DETERMINING MOLECULAR WEIGHTS. By HENRY BILTZ, Privatdocent at the University of Greifswald. Translated (with the author's sanction) by HARRY C. JONES, Associate in Physical Chemistry in Johns Hopkins University, and STEPHEN H. KING, M.D., Harvard University. Easton, Pa.: Chemical Publishing Co. 1899. 230 pages. Price, $2.00.

The German edition of this work was reviewed in this JOURNAL (**20**, 434) and its character fully described. In the translation some additions and changes, suggested by the author, have been made, and the work has been brought up to date. Its value as a text-book and laboratory guide can be best described by an extract from the translators' preface. "It can be fairly claimed that there is no book in English, and probably not in any other language, which deals with the problem of molecular weight determinations as satisfactorily as this recent publication by Biltz. We believe that the book will not only be useful in the laboratory, but, on account of its method of treatment, will also prove to be of service as a book of reference to the literature of molecular weight determinations."

J. E. G.